Investigation of Nanostructured Semiconducting Metal Oxide and Conducting Polymer Thin Films for Gas Sensing Applications

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

Abu Zafar Md Sadek
B.Sc.Eng. (Electrical and Electronic Engineering), Bangladesh University of Engineering & Technology (BUET), Dhaka, Bangladesh
M.Eng. (Telecommunications), The University of Melbourne, Australia

School of Electrical and Computer Engineering
RMIT University, Melbourne, Australia

April, 2008
AUTHOR’S DECLARATION

April, 2008.

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; and, any editorial work, paid or unpaid, carried out by a third party is acknowledged.

________________________
Abu Zafar Md Sadek
ACKNOWLEDGEMENTS

I would like to thank my senior supervisor Prof. Wojtek Wlodarski for providing me with the opportunity to conduct my PhD and for his advice, support and constructive feedback throughout my time at RMIT University. Special thanks to my second supervisor, Dr. Kourosh Kalantar-zadeh for his ever positive attitude and encouragement for me to pursue this research were pertinent to its completion.

I wish to thank current and former students within the Sensor Technology Group: Dr. Adrian Trinchi, Dr. David Powell, Dr. Samuel Ippolito, Dr. Glenn Matthews, Mr. Sasikaran Kandasamy, Mrs. Li Lin Li, Mr. Alexandru Fechete, Miss Joy Tan, Mrs. Rashidah Arsat, Mrs. Mahnaz Safei, Mr. Michael Breedon, Mr. Chen Zhang, Mr. Laith Al-Mashat, Mr. Hanif, Mr. Rick for providing a friendly and relaxed atmosphere for conducting research.

I would also like to take this opportunity to thank several people, without whom this research would not have been possible. I am very grateful to Prof. Richard Kaner and Ms. Cristina Baker of the Department of Chemistry and Biochemistry, UCLA, Los Angeles, and Prof. Koo Shin of the Department of Applied Chemistry, Sejong University, Seoul, Korea for their extensive assistance in polyaniline nanofibers and polyaniline/metal oxide nanocomposite synthesis. I would also like to thank Prof. Z. L. Wang and Dr. William Hughes of the School of Materials Science and Engineering, Georgia Tech, Georgia, Dr. Supab Chooopun of the Chiangmai University, Thailand and Prof. Yangshiang Li and Mr. Xiaofeng Yu of the Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China for their extensive assistance in ZnO nanobelts and nanorods synthesis. Additionally, I would like to thank Mr. Philip Francis of the Department of Applied Physics, RMIT University, for his input and help in organising SEM measurements.
I acknowledge the Commonwealth Government for providing me with financial support through their Australian Postgraduate Award (APA) scholarship program. I also acknowledge the faculty and staff of the School of Electrical and Computer Engineering at RMIT University. I am grateful to the technical staff of the school and MMTC for their assistance in fabrication technology, design and measurements systems and general technical advice.

I would like to thank Australian Research Council Nanotechnology Network (ARCNN) for proving financial support to present my papers at the 2006 and 2008 International Conference on Nanoscience and Nanotechnology (ICONN) in Brisbane and Melbourne, respectively.

I would also like to take this opportunity to express my sincerest love and thanks to my parents, my wife Shima, my brothers and sisters and my close friends. Their love, support and understanding and encouragement in undertaking a PhD are enormous.
In this thesis, the author developed and investigated nanostructured materials based Surface Acoustic Wave (SAW) and conductometric devices for gas sensing applications. The nanostructured material synthesis, device fabrication and their gas sensing performance have been undertaken. The investigated SAW structures are based on 64° YX LiNbO₃ and 36° YX LiTaO₃ substrates, with a piezoelectric zinc oxide (ZnO) intermediate layer. The conductometric structures are based on sapphire substrates. A variety of nanostructured materials were investigated as gas sensing elements, these are: ZnO nanorods and nanobelts, TiO₂ and gold (Au) doped TiO₂ nanoparticles, polyaniline nanofibers and polyaniline/metal oxide nanocomposites fibers. The developed nanostructured materials based sensors have high surface to volume ratio and achieved high sensitivity towards different gas species.

Thermal evaporation and radio frequency (RF) sputtering methods were used to synthesize and deposit ZnO nanobelts whereas ZnO nanorods were fabricated using a hydrothermal method. Polyaniline nanofibers and its nanocomposites with metal oxides were synthesized with rapidly mixed reaction method. All of the nanostructured materials synthesized by the author have at list one lateral dimension less than 100 nm. Nanostructural characterization techniques were employed to extract important information of gas sensitive films such as their structural morphology, surface topography, and material orientation. This information was required to understand the properties of nanostructured materials and link its properties to their gas sensing characteristics.

Structural characterization techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction spectroscopy (XRD) revealed that the developed ZnO nanobelts and nanorods thin films have single crystal, one-
dimensional nanostructures. The gas sensing results reveal that ZnO nanorod based sensors are more sensitive towards H₂, NO₂ and CO gas species than ZnO nanobelt based sensors due to nanorods well-aligned orientation to the substrate and nanorod based films high porosity. The developed ZnO nanobelt and nanorod based sensors have lower optimum operating temperature and higher sensitivity than conventional polycrystalline ZnO based gas sensors. The particle or grain size of a conventional polycrystalline zinc oxide gas sensor is considerably greater than the depth of the surface space charge region, thus, electrical conduction is controlled by the grain boundaries. However, as synthesized ZnO nanobelts and nanorods have greatly reduced dimensions (ZnO nanorods: average diameters 90 nm, ZnO nanobelts: average thickness 10 to 20 nm and average width 50 to 70 nm) which are comparable to the depletion layer depth. Thus, oxygen adsorption to the nanobelts and nanorods has lead to a complete depletion of conduction-band electrons with a large variation in resistance.

Micro-nano characterisation results revealed that sol-gel prepared gold doped TiO₂ film contains gold nanoparticles distributed on the surface having 10 nm average diameters with a film porosity of 37%. The gas sensing results revealed that gold nanoparticles addition to the TiO₂ have increased the sensor response towards H₂ by 1 kHz and decreased optimum operational temperature approximately 15°C. It is therefore supposed that the Au nanoparticles have an enhancing effect on the catalytic activity of TiO₂ for H₂ sensing in SAW device.

Hydrochloric acid (HCl) and camphor sulfonic acid (CSA) were used in the synthesis to obtain 30 and 50 nm average diameter polyaniline nanofibers. These polyaniline nanofibers were employed to developed polyaniline nanofibers/ZnO/SAW and conductometric sensors to operate at room temperature. It is the author’s best knowledge that he was the first to investigate and link polyaniline nanofibers diameters towards hydrogen gas sensing responses and found that camphor sulphonic acid (CSA) doped polyaniline nanofiber (average 50 nm diameter) based sensors have higher sensitivity towards H₂ than HCl doped polyaniline nanofiber (average 30 nm diameter) based sensors. However, the response and recovery were faster for the 30 nm diameter HCl doped nanofibers than that of the 50 nm diameter nanofibers. Additionally, to the author’s best knowledge, for the first time comparison between doped and dedoped nanofiber sensors responses have been investigated during this PhD work. Doped polyaniline nanofibers based sensor has higher sensitivity than that of dedoped.
The author also extended his research to successfully develop polyaniline/metal oxide nanocomposites/ZnO/SAW structures for room temperature gas sensing applications. The author's investigations revealed that polyaniline/In$_2$O$_3$ nanocomposite based sensors produced stable and stronger response towards gas species than other polyaniline/metal oxide nanocomposite based sensors. The gas sensing performance of the investigated nanostructured materials/SAW and conductometric structures provide a way for further investigation to future commercialization of these types of sensors.
CONTENTS

Chapter 1 ......................................................................................................................... 1
  Introduction ....................................................................................................................... 1
    1.1 Motivation .................................................................................................................. 1
      1.1.1 Fundamentals of Nanotechnology ....................................................................... 5
      1.1.2 Emergence of Nanotechnology ........................................................................... 5
      1.1.3 Nanotechnology Enabled Sensors ........................................................................ 6
      1.1.4 Gas Sensor Applications ..................................................................................... 7
      1.1.5 Applications Pertaining to This Research ........................................................... 8
    1.2 Gas Sensor ................................................................................................................. 10
      1.2.1 Different types of Gas Sensor .............................................................................. 10
        1.2.1.1 Classification Based on Transduction Principles ....................................... 11
        1.2.1.2 Classification Based on Sensing Materials .............................................. 16
    1.3 Objectives ................................................................................................................. 18
    1.4 Outcomes and Author’s Achievements .................................................................... 20
    1.5 Thesis Organisation ................................................................................................. 22
    REFERENCES .................................................................................................................. 24

Chapter 2 ......................................................................................................................... 29
  Gas Sensing Fundamentals and Literature Review ......................................................... 29
    2.1 Introduction ............................................................................................................... 29
    2.2 Current Status of Nanostructured Material Based Gas Sensors ............................. 30
      2.2.1 Review on Nanostructured Metal Oxide Sensors ............................................ 31
        2.2.1.1 Nanostructured ZnO Sensors ....................................................................... 31
        2.2.1.2 Nanostructured SnO₂ Sensors .................................................................... 32
### 2.2.1 Nanostructured Sensors

2.2.1.3 Nanostructured TiO$_2$ Sensors ............................................................... 33
2.2.1.4 Nanostructured MoO$_3$ Sensors ............................................................. 33
2.2.1.5 Nanostructured In$_2$O$_3$ Sensors ............................................................ 34
2.2.1.6 Nanostructured WO$_3$ Sensors ............................................................... 34

#### 2.2.2 Review on Nanostructured Polymer Sensors

2.2.2.1 Polyaniline Nanofiber Sensors ............................................................... 35

#### 2.2.3 Review on Polymer/Semiconducting Metal Oxide Nanocomposites

Gas Sensors ........................................................................................................ 37

### 2.3 Gas Sensing Mechanism of MOS Sensors

2.3.1 Oxygen Response Mechanism: Adsorption Model ....................................... 39
2.3.2 Surface Conductance in Semiconducting Oxide Films .................................. 40

### 2.4 Gas Sensing Mechanism of Polymer Based Sensors

2.4.1 Conductometric Sensitivity ........................................................................ 69
2.4.2 Mass Sensitivity .......................................................................................... 73

### 2.5 Summary

2.5 Summary ........................................................................................................ 48

### REFERENCES

<table>
<thead>
<tr>
<th>REFERENCES</th>
<th>49</th>
</tr>
</thead>
</table>

---

### Chapter 3

#### Theoretical Background of SAW Sensors

3.1 Introduction .................................................................................................... 57

3.2 Fundamentals of Surface Acoustic Wave Sensors .......................................... 58

3.2.1 Overview of Acoustic Wave Devices ......................................................... 58
3.2.2 Piezoelectric Substrate Materials ............................................................... 58
3.2.3 Surface Acoustic Wave Devices .................................................................. 59

3.3 Theoretical Analysis of Acoustics Waves ...................................................... 62

3.4 Principles of Operation for Surface Acoustic Wave Sensors ......................... 66

3.4.1 Conductometric Sensitivity ........................................................................ 69
3.4.2 Mass Sensitivity .......................................................................................... 73

3.5 Proposed Layered SAW Gas Sensor Structures ............................................ 74

3.6 Summary ........................................................................................................ 76

#### REFERENCES

<table>
<thead>
<tr>
<th>REFERENCES</th>
<th>78</th>
</tr>
</thead>
</table>

---

### Chapter 4

#### Fabrication of SAW and Conductometric Substrates

4.1 Introduction .................................................................................................... 82

4.2 SAW Transducer Fabrication Process ............................................................. 83

4.2.1 Photolithographic Mask ............................................................................ 83
4.2.2 Sample Preparation .................................................................................... 83
Chapter 5 ........................................................................................................... 92
Nanostructured Material Synthesis ................................................................. 92
  5.1 Introduction ................................................................................................ 92
  5.2 Fundamentals for Film Growth ................................................................. 93
  5.3 Methods for Achieving Nanostructured Materials ..................................... 94
      5.3.1 Vapor-Liquid-Solid (VLS) Growth ...................................................... 95
      5.3.2 Vapor-Solid (VS) Growth .................................................................. 96
  5.4 Synthesis of ZnO Nanostructures ............................................................. 97
      5.4.1 ZnO Nanobelt: Thermal Evaporation Method ..................................... 97
      5.4.2 ZnO Nanobelt: RF Sputtering ............................................................. 99
      5.4.3 ZnO Nanorod: Hydrothermal Method ............................................... 100
  5.5 Synthesis of TiO$_2$ Nanoparticles: Sol-gel Method .................................. 100
  5.6 Synthesis of Polyaniline Nanofiber and its Composite ............................ 102
      5.6.1 Polyaniline Nanofiber: Rapidly Mixed Method ................................. 102
      5.6.2 Polyaniline Nanofiber: Electrochemical Method ................................ 104
      5.6.3 Polyaniline/semiconducting Metal Oxides Nanocomposite Fibres: Chemical Polymerization ................................................................. 105
  5.7 Summary .................................................................................................... 106
REFERENCES ........................................................................................................ 107

Chapter 6 ......................................................................................................... 112
Micro-nano Characterisation Methods & Results ............................................. 112
  6.1 Introduction ................................................................................................ 112
  6.2 Different Micro-nano characterisation Techniques ..................................... 113
      6.2.1 Scanning Electron Microscopy (SEM) ............................................... 114
Chapter 7......................................................................................................... 143
Sensor Testing Set-up and Results.................................................................143
  7.1 Introduction .........................................................................................143
  7.2 Electrical Measurement Set-up............................................................144
    7.2.1 SAW Based Gas Sensor Testing Set-up.............................................144
    7.2.2 Conductometric Sensing Measurement Set-up ....................................147
    7.2.3 Gas Delivery and Gas Cell Set-up......................................................148
    7.2.4 Data Acquisition System and Testing Procedure...............................150
  7.3 Gas Sensing Results ............................................................................150
    7.3.1 Thermally Evaporated ZnO Nanobelt Based SAW Sensors...............151
    7.3.2 RF Sputtered ZnO Nanobelt Based Conductometric Sensors ..........155
    7.3.3 Hydrothermally Grown ZnO Nanorod Based SAW Sensors...............160
    7.3.4 Sol-gel Prepared TiO$_2$ Nanoparticle Based SAW Sensor .................165
    7.3.5 Polyaniline Nanofiber Based SAW Sensor ........................................168
    7.3.6 Polyaniline Nanofiber Based SAW Sensor: Electrodeposition ..........173
    7.3.7 Polyaniline Nanofiber Based Conductometric Sensor ......................175
    7.3.8 Polyaniline/Metal Oxide Nanocomposite Based SAW Sensor ............177
  7.4 Summary ............................................................................................183
REFERENCES ...............................................................................................186
Chapter 8 ........................................................................................................ 189
  Conclusions and Future Work .......................................................................................... 189
    8.1 Conclusions ........................................................................................................ 190
    8.2 Future Work ........................................................................................................ 193

Appendix A ...................................................................................................... 194
  List of Author’s Publications ..................................................................................... 194
    A.1 Refereed Journals ............................................................................................ 194
    A.2 Conference Papers ............................................................................................ 195
LIST OF FIGURES

Figure 1.1: Schematic of a feedback sensing control system .................................................................................... 2
Figure 1.2: Conductometric transducer .................................................................................................................. 12
Figure 1.3: Configuration of quartz crystal microbalance sensor device [48]............................................................ 12
Figure 1.4: Configuration of surface acoustic wave sensor device. ............................................................................ 13
Figure 1.5: Cross structure of the thin-film bulk acoustic resonator (TFBAR) [57].......................................................... 14
Figure 2.1: Schematic diagram of a traditional polyaniline thin film (left) and nanofibers (right) exposed to gas molecules (arrows) [45].................................................................................................. 35
Figure 2.2: Schematic diagram of polyaniline nanofiber based films with different thickness [45]. ................................................................. 36
Figure 2.3: Schematic representation of a porous sensing layer with geometry and energy band (\(\lambda_D\) Debye length, \(X_g\) grain size) [75].................................................................................................................. 42
Figure 2.4: Schematic representation of resistance on nanorod boundaries and contacts. (Dark areas refer to the space-charge region).................................................................................................................. 43
Figure 2.5: Schematic representation of a sensing layer based on nanorods of semiconducting oxide showing inter-rod contact resistance.................................................................................................................. 44
Figure 2.6: Schematic diagram of a porous ZnO nanorod based film exposed to gas molecules (arrow).................................................................................................................. 44
Figure 2.7: Polyaniline in the emeraldine oxidation state can exist in either its undoped (top), intermediate bipolaron (middle) or fully doped acid form (bottom)............. 46
Figure 2.8: Possible mechanism for hydrogen interaction with doped polyaniline where A- represents the counteranion [98]. .................................................................................................................. 48
Figure 3.1: A schematic diagram of a SAW device. .................................................................................................... 59
Figure 3.2: Rayleigh type surface acoustic wave [7].................................................................................................... 61
Figure 3.3: Shear horizontal type surface acoustic wave [7]. ....................................................................................... 61
Figure 3.4: Relations among mechanical and electrical variables for a piezoelectric crystal. The numbers in square brackets and parentheses show the ranks of the tensors. ................................................................. 63

Figure 3.5: Schematic of a conventional SAW gas sensor structure. ......................................................... 66

Figure 3.6: Surface wave velocity and attenuation as a function of layer conductivity. ........69

Figure 3.7: Schematic of the proposed layered SAW structure......................................................... 75

Figure 4.1: Orientation of lithium niobate (64° YX LiNbO₃) with shear horizontal SAW delay line devices. ................................................................. 85

Figure 4.2: Summary of the photolithography process................................................................. 85

Figure 4.3: A fabricated 64° YX LiNbO₃ SAW transducer, showing two sets of identical resonators. ................................................................. 86

Figure 4.4: A schematic representation of the sputtering system at MMTC, RMIT University. ........................................................................ 88

Figure 4.5: Mask used to fabricate the alumina based conductometric transducer, IDT electrodes (left), heater (right). ................................................................. 89

Figure 5.1: Schematic illustration of three basic models of initial nucleation in the film growth [1]. ........................................................................ 93

Figure 5.2: Schematic showing the principal steps of the vapour-liquid-solid (VLS) growth technique: from initial nucleation to continued growth ........................................................................ 96

Figure 5.3: Schematic diagram of experimental apparatus for growth of oxide nanostructures in thermal evaporation method ........................................................................ 98

Figure 5.4: Traditional polymerization of polyaniline. ...................................................................... 102

Figure 5.5: Polyaniline nanofiber diameter with different synthesis acids in rapidly mixed polymerization method. ................................................................. 102

Figure 5.6: Schematic showing rapidly mixed polymerization of polyaniline nanofibers. ... 104

Figure 5.7: The electro-polymerisation cell. ........................................................................ 105

Figure 6.1: Schematic diagram of an SEM set-up [4]. ........................................................................ 115

Figure 6.2: Schematic diagram of a transmission electron microscope (TEM) [4]. ................ 117

Figure 6.3: A schematic diagram of an XRD set-up ........................................................................ 118

Figure 6.4: SEM image of sputtered ZnO thin film growth on bare LiNbO₃ (left) and gold (right) [9]. ........................................................................ 119

Figure 6.5: XRD analysis of ZnO seed layer/intermediate layer on 64° YX LiNbO₃ [9]. ...... 119

Figure 6.6: SEM image of thermally deposited ZnO nanobelts [15]. ........................................ 120

Figure 6.7: (a) TEM image of thermally deposited ZnO nanobelts, (b) High resolution TEM image with the incident electron perpendicular to the top surface of the nanobelt [1]. ........................................................................ 120

Figure 6.8: XRD pattern of thermally deposited ZnO nanobelts [15] ........................................ 121

Figure 6.9: SEM image of ZnO nanobelts on alumina substrate in 5 µm scale [17]. .......... 122
Figure 6.10: SEM image of ZnO nanobelts on alumina substrate in 1 µm scale [17] .............. 122
Figure 6.11: (a) TEM bright field image of a ZnO nanobelt, the inset is a zoom of [100] spot, (b) associated SADP of ZnO layer [16] ......................................................... 123
Figure 6.12: SEM image of ZnO nanorods on ZnO/64° YX LiNbO₃ substrate in 5 µm scale [20] ............................................................................................................ 123
Figure 6.13: SEM image of ZnO nanorods on the interface of LiNbO₃ (bottom corner) and gold IDT’s (top corner) in 500 nm scale [20] ........................................ 124
Figure 6.14: SEM image of ZnO nanorods growth on gold (Au) IDT’s in 500 nm scale [20] 124
Figure 6.15: SEM image of ZnO nanorods growth on LiNbO₃ in 500 nm scale [20] ........ 124
Figure 6.16: XRD pattern of hydrothermally deposited ZnO nanorods. .......................... 125
Figure 6.17: XRD spectra of TiO₂ and TiO₂-Au films annealed up to 300°C [22] .............. 126
Figure 6.18: TEM images of Au nanoparticles as synthesized in water (left) and inside the TiO₂ matrix (right) heated up to 300°C [22] ................................. 127
Figure 6.19: Optical absorbance spectra of Au nanoparticles in solution, of TiO₂-Au film and of TiO₂ film [22] ................................................................. 127
Figure 6.20: SEM image of chemically polymerized HCl doped polyaniline nanofibers on a SAW substrate [27] ............................................................. 128
Figure 6.21: SEM image of chemically polymerized HCl doped polyaniline nanofibers on the sapphire substrate [28] ......................................................... 129
Figure 6.22: TEM image of chemically polymerized HCl doped polyaniline nanofibers on lacy carbon grid [29] ................................................................. 129
Figure 6.23: TEM image of chemically polymerized CSA doped polyaniline nanofibers on carbon film grid [29] ................................................................. 129
Figure 6.24: SEM images of electrochemically grown polyaniline nanofibers onto a gold surface: growth sequence from (a) to (d) [30] ................................................ 130
Figure 6.25: Close-up SEM image of a polyaniline/In₂O₃ nanofiber matt [35] ............... 131
Figure 6.26: TEM image of a polyaniline/In₂O₃ nanofiber matt [35] .............................. 132
Figure 6.27: Powder X-ray diffraction pattern of a polyaniline/In₂O₃ nanofiber composite (top) and a bar graph for pure In₂O₃ from the JC-PDS database (bottom) [35] ........................................................................................................ 132
Figure 6.28: SEM image of polyaniline/WO₃ nanofibers [37] ........................................... 133
Figure 6.29: TEM image of polyaniline/WO₃ nanofiber composite [37] .......................... 133
Figure 6.30: XRD image of polyaniline/WO₃ nanofiber composite [37] .......................... 134
Figure 6.31: SEM image of polyaniline/SnO₂ nanofibers [38] ........................................ 134
Figure 6.32: TEM image of polyaniline/SnO₂ nanofibers [38] ........................................ 135
Figure 6.33: XRD characterization of polyaniline/SnO₂ nanofibers (top) and standard JCPDS of SnO₂ (below) [38] ................................................................. 135
Figure 7.1: Feedback loop oscillator configuration ......................................................... 145
Figure 7.2: Experimental set up for nanomaterial based SAW gas sensors..........................147
Figure 7.3: Experimental set up for nanomaterial based conductometric gas sensors........148
Figure 7.4: A schematic of the gas cell set-up........................................................................149
Figure 7.5: Frequency and phase response of the bare 36° YX LiTaO₃ and ZnO nanobelts
layer on 36° YX LiTaO₃ in ambient conditions.................................................................151
Figure 7.6: Frequency and phase response of the bare 64° YX LiNbO₃ and ZnO nanobelts
layer on 64° YX LiNbO₃ in ambient conditions.................................................................152
Figure 7.7: Response of a 36° YX LiTaO₃ SAW based sensor towards different
concentrations of H₂ gas at 185° C.......................................................................................153
Figure 7.8: Frequency shift versus H₂ concentration (%)......................................................153
Figure 7.9: Response of a 64° YX LiNbO₃ SAW based sensor towards different
concentrations of NO₂ gas at 160° C....................................................................................153
Figure 7.10: Frequency shift versus NO₂ gas concentration (ppm).........................................154
Figure 7.11: Dynamic response of the conductometric sensor to different H₂ gas
concentrations in synthetic air at 350 and 420°C [11].........................................................157
Figure 7.12: Dynamic response of the conductometric sensor to different NO₂ gas
concentrations in synthetic air at 300 and 325°C [11].........................................................157
Figure 7.13: Sensitivity vs operating temperature for 1% H₂ and 8.5 ppm NO₂ gas
concentrations in synthetic air [11]......................................................................................157
Figure 7.14: Sensitivity vs operating temperature for 1% propene concentration in
synthetic air [11]..................................................................................................................158
Figure 7.15: Dynamic response of the conductometric sensor to different H₂ gas
concentrations in synthetic air at 385°C [11]......................................................................158
Figure 7.16: Dynamic response of the conductometric sensor to different NO₂ gas
concentrations in synthetic air at 350°C [11]......................................................................158
Figure 7.17: Dynamic response of the conductometric sensor to different propene gas
concentrations in synthetic air at 370°C [11]......................................................................159
Figure 7.18: Frequency and phase response of the bare 64° YX LiNbO₃, ZnO seed layer
on 64° YX LiNbO₃ and ZnO nanorods on ZnO/64° YX LiNbO₃ in ambient
conditions..............................................................................................................................160
Figure 7.19: Dynamic response of the sensor to different H₂ gas concentrations in
synthetic air at 265°C [13]....................................................................................................161
Figure 7.20: Frequency shift (kHz) versus H₂ gas concentration (%) in synthetic air at
265°C [13]............................................................................................................................161
Figure 7.21: Dynamic response of the sensor to different CO gas concentrations in
synthetic air at 265°C............................................................................................................162
Figure 7.22: Frequency shift versus CO concentration (ppm)...............................................162
Figure 7.23: Dynamic response of the sensor to different NO₂ gas concentrations in synthetic air at 265°C.......................... 162
Figure 7.24: Frequency shift (kHz) versus NO₂ concentrations in synthetic air at 265°C.......................... 163
Figure 7.25: Frequency shift (kHz) versus operating temperature for 0.15% H₂, 425 ppb NO₂ and 150 ppm CO concentrations in synthetic air.......................... 163
Figure 7.26: Frequency and phase response of the TiO₂ and gold doped TiO₂ layer on 64° YX LiNbO₃ in ambient conditions.......................... 165
Figure 7.27: Dynamic response of a TiO₂ based 64° YX LiNbO₃ SAW sensor towards H₂ at 230°C.......................... 166
Figure 7.28: Dynamic response of a TiO₂-Au based 64° YX LiNbO₃ SAW sensor towards H₂ at 230°C.......................... 166
Figure 7.29: Frequency shift versus operational temperature for TiO₂ and TiO₂-Au based 64° YX LiNbO₃ SAW sensors towards H₂.......................... 167
Figure 7.30: Frequency and phase response of the layered ZnO/64° YX LiNbO₃ substrate, and HCl and CSA doped polyaniline nanofiber layers on ZnO/64° YX LiNbO₃ in ambient conditions.......................... 168
Figure 7.31: Dynamic response of HCl doped polyaniline nanofiber based ZnO/64° YX LiNbO₃ SAW sensor towards H₂ at room temperature [14].......................... 169
Figure 7.32: Dynamic response of a CSA doped polyaniline nanofiber based ZnO/64° YX LiNbO₃ SAW sensor towards H₂ at room temperature [14].......................... 169
Figure 7.33: Frequency shift (kHz) versus H₂ gas concentrations (%) at room temperature [14].......................... 170
Figure 7.34: Response and recovery times (second) versus H₂ gas concentrations (%) at room temperature [14].......................... 170
Figure 7.35: Sensitivity comparison of CSA doped polyaniline nanofiber sensors when randomly drop-cast over five SAW substrates. Average thickness variation of the films is ±0.4 µm.......................... 173
Figure 7.36: Frequency and phase response of the bare 64° YX LiNbO₃ SAW substrate and electro-polymerized polyaniline nanofiber layer on 64° YX LiNbO₃ in ambient conditions.......................... 173
Figure 7.37: SEM image of polyaniline nanofibers grown onto a SAW substrate. ................ 174
Figure 7.38: Frequency shift (kHz) versus H₂ gas concentration (%) at room temperature 175
Figure 7.39: Dynamic response of the dedoped polyaniline nanofiber based conductometric sensor to different H₂ gas concentrations in synthetic air [19].......................... 175
Figure 7.40: Dynamic response of the doped polyaniline nanofiber based conductometric sensor to different H₂ gas concentrations in synthetic air [19].......................... 176
Figure 7.41: Sensitivity of doped and dedoped polyaniline nanofiber sensors towards different concentrations of H₂ in synthetic air [19].......................... 176
Figure 7.42: Frequency and phase response of the polyaniline/metal oxide nanocomposite/64° YX LiNbO₃ SAW substrates in ambient conditions........ 178

Figure 7.43: Dynamic response of the SAW sensor towards different concentrations of H₂ at room temperature [25]. ........................................................................................................... 178

Figure 7.44: Dynamic response of the SAW sensor towards different concentrations of CO at room temperature [25]. ........................................................................................................ 179

Figure 7.45: Dynamic response of the SAW sensor towards different concentrations of NO₂ at room temperature [25]. ........................................................................................................ 179

Figure 7.46: Frequency shift (kHz) versus H₂ gas concentration (%) at room temperature for polyaniline/ In₂O₃, Polyaniline/ WO₃ and Polyaniline/ SnO₂ nanocomposite based gas sensors. ........................................... 180

Figure 7.47: Dynamic response of a polyaniline/WO₃ nanofiber composite based 64° YX LiNbO₃ SAW sensor towards H₂ at room temperature................................................. 181

Figure 7.48: Dynamic response of a polyaniline/SnO₂ nanofiber based layered ZnO/64° YX LiNbO₃ SAW sensor towards H₂ at room temperature. ................................. 181
LIST OF TABLES

Table 3.1: Comparison of different piezoelectric substrate materials ........................................59
Table 6.1: Values of thickness, refractive index and porosity of TiO$_2$ and TiO$_2$-au films 
measured by ellipsometry ........................................................................................................128
Chapter 1

Introduction

1.1 Motivation

Many industrial and commercial activities involve the monitoring and control of the environment, with applications ranging from domestic gas alarms and medical diagnostic apparatus to safety, security, and chemical plant instrumentation. Most of these applications require precise real time monitoring and control to increase productivity, maintain health and safety, and keep environmental pollution within limits. However, the largest obstacle to achieve improved industrial process or environmental control often lies at the interface between the system and the environment to be monitored, i.e. the sensor. Without sensors, significant advances in industrial and environmental monitoring, control and instrumentation will not be possible.

Figure 1.1 shows the standard operation of a feedback sensing control system. In this example, the sensor transforms the chemical signal into electrical signals in order to be processed by the microprocessor, while the actuator provides feedback to the environment by transforming the electrical signal to a chemical signal. Unlike control electronics, sensors
have to be exposed directly to the environment for interaction with the target species. Even apparently benign atmosphere may contain corrosive or contaminating species, which can seriously interfere with sensor operation and eventually reduce sensor performances. Thus, sensor technology has continued to lag, particularly with regards to achieving adequate sensitivity, selectivity, reproducibility, and stability at reasonable cost [1-2].

Gases are key targets in many industrial and domestic activities requiring precise measurement or control. This has been stimulated by a series of clean air laws, which have or are being legislated on the international, national, state and local levels. These often require in-situ continuous monitoring of air quality and the rates of emissions of specific chemical species.

Thus, new gas sensors are required to meet increasingly stringent legal restrictions and industrial health and safety requirements, as well as for environmental monitoring, automotive applications and for manufacturing process control. To meet these demands, the sensitivity, selectivity and stability of conventional sensors need to be drastically improved. To achieve these goals attention is being focused on several approaches such as research on novel sensing materials, use of catalysts and promoters, surface modification, multi-sensor array systems, data processing methods (FFT and wavelet transform, pattern recognition), fabrication techniques, optimization of sensor performance and the use of nanotechnology. Many different transducing platforms are being pursued for gas sensing including electrochemical, chemo-resistive (conductometric), mass spectroscopic, optical and acoustic. In this work, the author has focused on mainly nanostructured material based acoustic wave and conductometric gas sensors.
Recently intense research activities have been devoted to the synthesis, structural characterization and investigation of physical properties of nanostructured materials. Due to size effects, nanostructured materials often exhibit novel physical properties and are of great interest for fundamental studies and for device applications [3]. Electrical, magnetic, optical and mechanical properties have all been observed to change at the nanoscale compared to those of the same material in bulk forms. Potential applications of nanostructured materials include: nano-sensors including highly sensitive gas sensors, bio-sensors, photo detectors, etc [4-7].

Nanostructured materials such as metal oxides in the form of nanoparticles, nanowires, nanorods and nanobelts [4, 8], conducting polymers in the form of nanofibers and nanowires [5], and carbon nanotubes [9], provide the opportunity to greatly increase the response of these materials based sensors, as sensor performance is directly related to granularity, porosity and ratio of surface area to volume of the sensing materials. It has been established that the sensitivity of semiconductor metal oxide and conducting polymers gas sensors increases with decreasing grain size [5,10], as the entire thickness of the sensitive layer can be affected by the reactions of the gas species. Thus, low dimensional nanostructured materials, which have an increased surface to volume ratio when compared to conventional polycrystalline structures, facilitate rapid diffusion of gases into and out of the materials’ nano- and microporosities, which in turn increases the reaction rate, resulting in faster sensor response and recovery.

Among the semiconductor metal oxides, ZnO was one of the earliest discovered and is the most widely applied gas sensing materials due to its high mobility of conduction electrons and good chemical and thermal stability [11]. Semiconducting zinc oxide in the form of nanobelts, nanorods and nanowires is of growing importance for the development of highly sensitive gas sensors. ZnO nanorods and nanobelts with hexagonal and rectangular cross section, respectively, have a distinct structural morphology (wurtzite family) and a uniform structure, are very promising for the development of stable gas sensors [12]. Additionally, nanobelts and nanorods form porous structure when deposited as thin films. Their large surface to volume ratios and nanoscale dimensions allow quick diffusion of gases into and out of the belt or rod, which increases the intensity of reactions resulting in high sensitivity and fast sensor response and recovery.

Conducting polymers are of increasing importance in the development of sensors due to their room temperature operation, low fabrication cost, ease of deposition onto a wide variety of substrates and their rich structural modification chemistry [13]. Among the family of conducting polymers, polyaniline is one of the most highly studied materials because of its
simple synthesis, environmental stability and straightforward non-redox doping/dedoping process to control conductivity [14]. Polyaniline nanofibers, with diameters in the 30-100 nm range, possess much larger surface to volume ratios [15] and permit easier addition of surface functionality and interaction compared with traditional polyaniline which is highly agglomerated. In addition, polyaniline nanofibers have a cylindrical morphology and form porous structures when deposited as thin films. This structure allows easy diffusion of gas molecules into and out of the film and the nano-scale fiber diameters lead to rapid diffusion of gas molecules into the polyaniline. As a result, most reports indicate that nanostructured polyaniline outperforms conventional polyaniline for gas sensing applications [16].

The sensitivity of conventional polyaniline thin film sensors depends on the film thickness [5]. On the other hand, sensitivity of a polyaniline nanofiber sensor is independent of film thickness, due to the porous structure of the film which leads to surface phenomena dominating the material response. This allows the fabrication of sensors with reproducible responses that have a large tolerance for thickness variation [5].

There is a growing interest to combine both organic and inorganic materials for applications in electronics and optics [17]. The combination of nanosized metal oxides and polyaniline has the potential to increase the sensitivity selectivity of the conducting polymer. Such composites can operate at room temperature and the selectivity towards different gas species can be controlled by the volume ratio of nanosized metal oxides. In addition, the composite may have better long term stability. The organic/inorganic nanocomposite materials are considered as bi-phase materials where the organic and inorganic phases are mixed at the nanometer scale. The properties of nanocomposite materials depend not only on the properties of their constituents but also on their combined morphology and interfacial characteristics [18].

The author’s focus in this PhD research is to develop highly sensitive nanostructured material based surface acoustic wave (SAW) and conductometric gas sensors to detect hydrogen (H₂), hydrocarbon, carbon monoxide (CO), and nitrogen dioxide (NO₂). Based on the critical review of literature, which will be presented in Chapter 2, the author made an informed decision to develop novel nanostructured ZnO (nanorods and nanobelts), polyaniline (nanofibers), and polyaniline/metal oxide (In₂O₃, WO₃, SnO₂) nanocomposites based SAW and conductometric sensors. Additionally, to the best knowledge of the author, the abovementioned nanostructured material thin films have never been comprehensively investigated on SAW substrates for gas sensing applications. This PhD research has led to many novel outcomes and contributions to the body of knowledge in the field of
semiconducting metal oxide, conducting polymers and organic/inorganic nanocomposite based sensors, highlighted by the publications listed in Appendix A.

1.1.1 Fundamentals of Nanotechnology

The Greek word “nano” (meaning dwarf) refers to a reduction of size, or time, by $10^{-9}$, which is one thousand times smaller than a micron. One nanometer (nm) is one billionth of a meter and it is $10^4$ times smaller than the diameter of a human hair [19]. Nanotechnology deals with small structures or small-sized materials in the nanometer range. In general, nanotechnology can be understood as a technology of design, fabrication and application of nanostructures and nanomaterials. Nanotechnology also includes fundamental understanding of physical properties and phenomena of nanomaterials and nanostructures. In the United States, nanotechnology has been defined as being “concerned with materials and systems whose structures and components exhibit novel and significantly improved physical, chemical and biological properties, phenomena and processes due to their nanoscale size” [20].

The essence of nanotechnology is the ability to work at the molecular level with atomic scale arrangements, to create large structures with fundamentally new molecular organization. The aim is to exploit the properties at nanoscale by gaining control of structures and devices at atomic, molecular, and supramolecular levels and learn to efficiently manufacture and use the devices [20].

The promise of nanoscale science and technology is based on the demonstrated fact that materials at the nanoscale have properties quite different from the materials in their bulk forms. Compared to bulk materials, it is demonstrated that nanostructured materials possess enhanced performance when they are used in similar applications [21].

1.1.2 Emergence of Nanotechnology

The trend toward the small began with the miniaturization of macro techniques, which led to the now well-established field of micro-technology. Electronics, optical, and mechanical micro-technologies have all profited from the smaller, smarter, and less costly devices that resulted from work with integrated circuits (ICs), fiber optics, other micro-optics, and micro-electromechanical systems (MEMS). As we continue to go smaller and work with these minuscule building blocks, there will be a convergence of these technologies called nanotechnology. The continued decrease in device dimensions has followed the well-known Moore’s law [22] which predicted in 1965 that the dimension of a device halves approximately every eighteen months and today’s transistors fall well in the nanometer range.
Nanotechnology is new, but research on nanometer scale is not new at all. The study of biological systems and the engineering of many materials such as colloidal dispersions, metallic quantum dots, and catalysts have been in the nanometer regime for centuries. For examples, the Chinese are known to use gold (Au) nanoparticles as an inorganic dye to introduce red colour into their ceramic porcelains more than thousand years ago [23]. The discovery of synthetic materials, such as carbon fullerenes [24], carbon nanotubes [25], and ordered mesoporous materials [26], has fuelled the research in nanotechnology and nanomaterials. Recent invention and development of characterization and manipulation techniques at the nanometer level also paced the advancement of nanotechnology and make it so compelling from scientific, industrial, business and political viewpoints.

1.1.3 Nanotechnology Enabled Sensors

Nanotechnology enables us to create functional materials, devices, and systems by controlling matter at the atomic and molecular scales and to exploit novel properties and phenomena [27]. In particular, nanotechnology offers a unique advantage to the sensor industry by manipulating/incorporating/fabricating/arranging materials at the molecular level, where sensing events occur. Nanostructured materials have a higher percentage of active surface atoms, which detect molecular events more effectively and maximize sensor output signal in comparison with polycrystalline material based thin film devices [28]. Thus, they offer a larger surface area for functionalization, which would greatly increase the number of binding sites for the detection of a specific analyte.

Additionally, each crystallite of the semiconducting metal oxide has an electron depleted surface layer of the depth of the Debye length ($\lambda_D$) which is modulated by the reactions with the gas species. If the diameter (D) of the crystallite decreases to be comparable to $2\lambda_D$, the whole crystallite is depleted in electrons, resulting in high sensitivity towards gas species [29]. As a result, nanotechnology offers devices with greater sensitivity and reliability than conventional semiconductor, electro-chemical and optical sensors [30-31].

Nanotechnology enabled sensors have the potential to replace traditional sensors for applications in many industries, among them transportation, communications, building and facilities, environmental, medicine, safety, and national security. Integrating nanostructures and nanomaterials with MEMS technology and microelectronics seems to yield highly sensitive and inexpensive sensors and currently many groups from around the world are exploring these opportunities. Many start-up companies are also working to develop the devices in an effort to be first movers in commercialisation. In the literature, numerous
nanostructured materials have been already reported to be usable as highly sensitive sensors for chemical and biological species [32].

Exploiting the advantages from nanotechnology to enhance sensor performances is not without challenges. Sensor manufacturers encounter difficulties in manufacturing nanostructures, controlling their behaviour from the nano to the macro scale, reading reliable responses, and compensating for small signal drifts. The development and integration of nanostructured materials with MEMS, must take into account the realities imposed by physics, chemistry, biology, materials science and engineering.

1.1.4 Gas Sensor Applications

The need for gas sensors is enormous but the interest, in recent years, has grown from awareness in climate change, global warming, robotics and chemical warfare attack. Gas concentration profiles of ambient air are required by scientists, policy makers and planners to enable them to make crucial decisions on managing and improving the environment. The use of chemical weapons against civilians by terrorist groups or fanatic individuals is not just horror fiction anymore, but an absolute real threat. Two sarin gas attacks in Matsumoto and Tokyo, Japan in 1994–1995 confirmed this horrible reality. Chemical warfare agents (CWAs) are highly dangerous for human health because of their colourlessness and toxicity. Therefore, fast and correct detection of CWAs is essential to protect human beings and animals [33].

Across the whole of manufacturing industry, from chemical plants and refineries to high technology electronic component production, a wide range of gas phase chemical measuring techniques are required for process and quality control, and safety monitoring in complex processes. The scope for specialized sensors in this area of applications is enormous but the demands on sensor reliability and stability are very high [34]. Another major application of gas sensors is combustion monitoring in oil and gas fired boilers in industry and power plant, as well as automobile engines. The method usually used is to monitor the exhaust gases for low NOX, and then control the fuel to air mixture on the basis of feedback from sensors. Both applications have grown from the requirement to conserve fuel and to minimize polluting emissions. To achieve this, gas sensor systems are required that are capable of in situ and real time gas concentration measurements.

Each application places various requirements on the sensor and sensing system. However, the aim remains the same: to achieve accurate and stable monitoring of the analyte in the range of parts per million (ppm) to parts per billion (ppb) concentrations [35].
The specific applications for sensing the gases pertaining to this body of work are discussed in the following section.

1.1.5 Applications Pertaining to This Research

As mentioned above, four gas species have been targeted in this research: hydrogen, nitrogen dioxide, hydrocarbons (propene) and carbon monoxide. In this section, the author introduces them, as well as the major applications for sensing them. Reasons as to why it is important to monitor them are provided to rationalise the author’s choice for monitoring them and developing the sensors based on nanostructured materials that are the subject of this thesis.

Hydrogen (H\textsubscript{2})

Much attention has, and is, being paid to the sensing of hydrogen, largely due to its potential use as a clean source of energy. Hydrogen burns cleanly, requires no fuel processor in fuel cells, and is extracted from renewable energy resources, e.g. electricity from solar cells [36]. It is the most attractive future energy source.

The primary physical hazards associated with hydrogen gas are its flammability and potential for explosions. This is because hydrogen forms flammable mixtures in air over a wide range of concentrations (4-75%) and very low energy is needed to ignite hydrogen-air mixtures [37]. Hence sensors are required to detect hydrogen leaks to warn of explosion hazards.

In addition, hydrogen is a major cause of metallic corrosion. Due to its small size, hydrogen molecules can penetrate into metals and affect properties such as strength and durability, resulting in embrittlement. Corrosion caused by hydrogen can have a great impact on steel, especially in gas pipelines and in aircraft. Other important applications for hydrogen sensors include: fire warning systems; leak detection and monitoring of process control systems in industries such as glass, and petroleum industries; hydrogen driven vehicles; and even in biomedical applications. Whilst the existing hydrogen sensors find numerous industrial applications, a key anticipated use for this is as a skin-temperature, bandage-like hydrogen sensor that could be placed on a newborn infant for the real-time transcutaneous monitoring of fatal bacterial infections [36].

Hydrocarbons (HCs)

In organic chemistry, a hydrocarbon (a combination of the words "hydrogen" and "carbon") is an organic compound consisting mainly of carbon and hydrogen. Hydrocarbons are of prime economic importance because they encompass the constituents of the major fossil
fuels and plastics, paraffin, waxes, solvents and oils [38]. However, the majority of hydrocarbons found naturally occur in crude oil, where decomposed organic matter provides an abundance of carbon and hydrogen which, when bonded can catenate to form seemingly limitless chains [39]. In urban pollution, hydrocarbons along with NOₓ and sunlight all contribute to the formation of tropospheric ozone that cause adverse effects such as greenhouse effect on environmental eco-system. Additionally, hydrocarbon vapours can be harmful if inhaled.

In this work, the author has chosen propene (C₃H₆) gas from the hydrocarbon group for sensing. It is the second member of the alkene class of hydrocarbons after ethene. At room temperature and pressure, propene is a gas. It is colourless, odourless and highly flammable. Propene is a major commodity in the petrochemicals industry and used as a fuel gas for various industrial processes [40]. The primary sources that have reported emissions of propene are paper mills, petroleum refineries, and crude petroleum and natural gas extraction plants. Propene can also be dangerous for humans as short-term exposure can result in dizziness, mild intoxication, and anaesthesia. Irritation of the eyes, tearing, coughing, and flushing of the face has also been noted in exposed individuals. In all these environments, selective and highly efficient sensors are required for operation at low temperature.

**Carbon monoxide (CO)**

Carbon monoxide is a colourless, odourless, and tasteless gas. It consists of one carbon atom covalently bonded to one oxygen atom. CO is the product of the incomplete combustion of carbon-containing compounds, notably in internal-combustion engines [41]. Carbon monoxide is a major industrial gas that has many applications in bulk chemicals manufacturing. It has significant fuel value, burning in air with a characteristic blue flame, producing carbon dioxide. However, CO is a toxic chemical, which is harmful to human health. CO poisons by entering the lungs via the normal breathing mechanism and displacing oxygen from the bloodstream. Interruption of the normal supply of oxygen puts at risk the functions of the heart and brain, and as a result influences vital functions of the body [42]. Such a toxic and dangerous gas requires early detection to prevent health hazards.

**Nitrogen dioxide (NO₂)**

Nitrogen dioxide (NO₂) is one of the several nitrogen oxides (NOₓ). It is a reddish-brown gas and has a characteristic sharp, biting odour. The most important source of NO₂ is the internal
combustion engine, which emits nitrogen oxides near people. The major industrial sources of NO\textsubscript{x} emission are pulp mills and power plants [43].

NO\textsubscript{2} is one of the most important air pollutants and a poison by inhalation. Symptoms of poisoning (lung edema) tend to appear several hours after one has inhaled a low but potentially fatal dose. Also, low concentrations (4 ppm) will anesthetize the nose, thus creating a potential for overexposure. Long-term exposure to NO\textsubscript{2} at concentrations above 40–100 µg/m\textsuperscript{3} causes adverse health effects [44]. Airborne NO\textsubscript{2} transforms to form gaseous nitric acid and toxic organic nitrates, which play a major role in atmospheric reactions, producing ground-level ozone - a major component of smog. Therefore, it is important to control the emission of such gases with stringent legal limits and also develop procedures for continuously monitoring these gases in ambient and industrial atmosphere.

1.2 Gas Sensor

A gas sensor can be described as a device, which upon exposure to a gas alters one or more of its physical properties (e.g. mass, electrical conductivity, or capacitance) in a way that can be measured and quantified directly or indirectly [45]. Structurally, every gas sensor consists of: a physical transducer and a sensitive layer. Usually, the sensitive layer which is in contact with the environment is laid down on top of the transducer platform. At the sensitive layer, the gas molecules interact chemically with the surface, producing a change in physical/chemical properties. These changes are measured by the transducer resulting in the output electrical signal [46].

Gas sensors can be classified according to their operating principle or material use, each class having different parameters. Additionally, it is possible to change the properties of the sensor by changing sensing material and its morphology or annealing temperature during manufacturing or operation of the sensor.

1.2.1 Different types of Gas Sensor

There is a multitude of sensors using a wide variety of methods and technologies with which gas species can be analysed both quantitatively and qualitatively. All of these methods aim to provide accurate, stable, high resolution, low cost sensing. Therefore when selecting an approach, it is essential to accounted for temperature, humidity, shock and vibrations. All these factors can greatly impact on the sensors’ performance [47]. One way to classify gas
sensors is by the transduction mechanism. Different transduction principles that can be used for gas sensing are:

- Conductometric
- Acoustic
- Optical

Gas sensors can be classified according to the materials used on the surface of the transducer, such as metal oxide semiconducting (MOS), conducting polymer etc. Besides, gas sensors can also be arranged by the chemical reaction that occurs at the interface. Although gas sensors are classified depending on the transducing platforms, sensing materials and the reaction types, classification can overlap. For example, metal oxide and conducting polymer based sensors can employ any transducing (conductometric or acoustic) platforms and hence are called conductometric or acoustic sensors.

The author will now explore some of the most common approaches for gas sensing, all of which rely on the interactions between the gas and the sensing materials. Although the sensors investigated in this thesis are the surface acoustic wave and conductometric types, this section also discusses some other more common approaches. Their respective advantages and disadvantages are also discussed.

### 1.2.1.1 Classification Based on Transduction Principles

#### Conductometric Gas Sensors

Conductometric sensors are one of the most commonly utilized devices for sensing applications. They are also known as chemiresistors and many commercialized sensors are based on this principle. The related technologies, including fabrication and measuring, are mature. Thick films, thin films, fibers and bulk materials can be utilized as the sensing elements of a chemiresistor and the output signal is resistance or current which are facile to measure. The chemiresistor is formed by patterning metal interdigital transducers (IDTs) fingers on any insulating substrate such as alumina and silicon as shown in Figure 1.2. The chemiresistor also has a micro-heater fabricated on the opposite side of the IDT pattern. Usually, semiconducting metal oxides and conducting polymers are chosen for the sensing materials as their conductivity is changed in presence of specific gas molecules. Conductometric sensors have very good linearity and can measure large or small gas concentrations (ppm to ppb ranges).
Bulk Acoustic Wave Sensors (BAW)

The first acoustic wave device commonly used for electronic applications was the Quartz Crystal Resonator (QCR). It consists of a thin disc of single crystal piezoelectric quartz which is cut along a certain crystallographic axis. The disc is then covered with thin gold electrode pattern on either side to excite acoustic waves using the piezoelectric effect. Both sides of the QCR are finally coated with polymer or any sensitive films using common techniques such as spray coating, growth of Langmuir-Blodgett films or self-assembled monolayers, as shown in Figure 1.3.

The first reported use of this device for sensing application was in 1959 by Sauerbrey [49]. When used as a sensor, this device is most commonly referred to as a quartz crystal microbalance (QCM) due to its predominant mass sensitivity. For operation in gas media it was shown that the fractional frequency change due to mass loading increases linearly with operating frequency [49]. The operating frequency of this device is given by the material, crystal orientation and plate thickness. Normal operating frequencies are in the range from 10 to 30 MHz. Since the device operates in thickness shear mode (TSM), it is also able to operate in liquid media with relatively little acoustic energy loss.
**Surface Acoustic Wave Sensors (SAW)**

Piezoelectric surface acoustic wave devices were first developed by White and Voltmer in 1965 [50]. In its basic configuration, there is an input interdigital transducer (IDT) and an output IDT fabricated on a planar piezoelectric substrate and separated by a gap, as shown in Figure 1.4. The spacing of the IDT fingers determines the wave length. Application of a varying voltage to the input IDT generates the acoustic wave. The acoustic wave generated by the input IDT travels through the region called the delay line and reaches the output IDT, where the mechanical displacements due to the acoustic waves create a voltage difference between the output IDT fingers [51].

The SAW devices are widely used as electronic filters, delay lines, and resonators in today’s communication systems. Although the telecommunication industry is the largest user of these devices, SAW based sensors have many attractive features to be explored for emerging technologies in automotive (torque, pressure sensor), medical (biosensor), industrial and environmental (vapor, gas, humidity sensor) applications [52]. The first SAW device for sensing applications was a Rayleigh type [53]. They are small, inexpensive, can easily be designed for responding to various measurands, have wide dynamic range, and are passive devices which can also be deployed as wireless units.

For sensing applications, the delay lines of SAW devices are coated with some bio/chemical coating, which reacts with the entity under analysis. Gas or chemical interaction changes the mass, conductivity and/or the physical properties of the sensitive layer, which influences the propagation of the surface waves. This interaction produces a shift in the resonant frequency of the SAW device. By measuring this frequency shift, a detailed analysis of the entity being sensed can be completed. In many cases a dual SAW set-up is used and the signal of the
sensor is mixed with a reference signal from an uncoated SAW to minimise unwanted environmental and temperature effects.

**Thin-film Bulk Acoustic Wave Resonator (TFBAR)**

The operating principle of TFBAR [54] is same as quartz crystal micro-balance with an extension of operational frequency to several GHz. The usual operating frequency of QCM is in the range of 10 to 30 MHz and surface acoustic wave devices are up to few GHz or more. For acoustic wave devices, it is assumed that the response to added mass, in terms of absolute frequency changes, increases with the square of the operating frequency [55]. This means that theoretically, the sensitivity of TFBAR device will be higher than the other acoustic devices and has the potential to sense the analyte concentrations at ppb level. Due to the extended operating frequency (GHz), TFBAR structures can greatly improve the performances of mass sensitive sensors.

Using Sauerbrey-Lostis approximation [49, 56] for the acoustic wave device, \( \frac{\Delta f}{f_o} = -\Delta m/m_o \), where the change \( \Delta f \) in the resonance frequency \( f_o \) caused by the incremental mass \( \Delta m \) of adsorbed analyte. The mass of the resonator, \( m_o = \rho_p S d \), and operating frequency \( f_o = \frac{v_p}{2d} \), where \( \rho_p \), \( S \), \( d \) and \( v_p \) are the density, surface area, thickness, and acoustic wave velocity, respectively. As a result, the fractional frequency shift due to adsorbed analyte will be given by the following equation:

\[
\Delta f = -\frac{v_p}{2\rho_p d^2} \left( \frac{\Delta m}{S} \right)
\]  

(1.1)

For a given \( \Delta m/S \), the frequency shift increases with the increase of acoustic wave velocity (i.e frequency) and the decrease of film thickness (\( d^2 \)). It can be concluded that both an increase of operational frequency and use of thin-film resonators strongly improve the response of TFBAR sensors.

![Cross structure of the thin-film bulk acoustic resonator (TFBAR)](image)

Researchers in Italy [57] have successfully fabricated TFBAR on a Si wafer using \( \text{Si}_3\text{N}_4/\text{AlN} \) membranes as shown in Figure 1.5. They deposited Pd and Co-tetra-phenyl-porphyrin thin
films by thermal evaporation to form TFBAR sensors and investigated the sensors performance towards H₂, CO and ethanol gases. They found that the developed sensors can detect gas concentrations in the ppb levels with a fast and repeatable response.

**Fibre Optic Gas Sensor**

Fibre optic sensors are a class of devices that use optical fibres to measure gas species concentration. In their simplest form, light is generated by a light source and is sent through an optical fibre. The light then returns through the optical fibre after modulation by the analytes/measurands under consideration and is captured by a photo detector [58]. There are three general classes of fibre optic sensors [59]:

- The first type is completely passive. A spectroscopic method can be used to detect individual types of gas species. This method involves sending a light beam directly through the optical fibre and analysing the light that is reflected or emitted by the gas species. The refractive index of the material at the tip of the optical fibre can be used to determine what phases (vapour or water) are present.

- The second class consist of a fibre optic sensor with a chemically interacting thin film attached to the fibre tip. This film is formulated to bind with certain types of chemicals. Gas species concentration can be found by measuring the colour of the thin film, the change in refractive index, or by measuring the fluorescence of the film.

- The third type of fibre optic sensor involves injecting a reagent near the fibre tip. This reagent reacts either chemically or biologically with the gas species. The reaction products are detected to give an estimate of the gas species concentration.

The main advantages of optical gas sensors are their low power consumption, detection of various chemicals at very low concentrations, immunity to the electro-magnetic interference (EMI) and possibility of performing remote sensing in hostile environments. The disadvantages include: limited ability to transmit light through the optical fibre over long distances; some organic pollutants are not easily differentiated using UV-visible spectroscopy; and the concentration range sensitivity may be limited.

**Infra-red (IR) Sensors**

Infra-red sensors are typically comprised of a source of infrared radiation, a detector, and a path between the detector and source that is exposed to the gas being sensed. When a gas is present in the path, it absorbs energy from the IR source, and the detector receives less radiation than without the gas presence. In general, IR sensors have unique infra-red absorption signatures in the 2-14 μm range. The uniqueness of the gas absorption spectra
enables identification and quantification of chemicals in liquid and gas mixtures with little interference from other gases [58].

The major advantages of these devices are: requiring less calibration than other sensors; immunity to contamination and poisoning; and ability to operate in continuous presence of gas. However, there are some major drawbacks such as: they can only monitor specific gases that have non-linear molecules; they can be affected by humidity and water; dust and dirt can coat the optics and impair the sensor response which is a concern in in-situ environments; and they are more expensive than the other types of sensors.

1.2.1.2 Classification Based on Sensing Materials

Metal Oxide Semiconductor Sensors (MOS)

Sensors based on semiconductor metal oxide (SMO) thin films are the most promising among solid state gas sensors, due to their small dimensions, low cost, on-line operation, and high compatibility with microelectronic processing [60]. They have been used extensively for gas sensing based on film conductivity changes [61-63]. Intense research and development have been conducted to design highly sensitive, selective and stable gas sensors since Seiyama first observed gas sensing effects in Zinc Oxide (ZnO) [64]. Later, the range of sensitive materials was extended to SnO₂, TiO₂, WO₃, In₂O₃ and other oxides. Semiconductor metal oxide based gas sensors are used for environmental and emission monitoring, automotive, domestic, industrial and medical applications.

The gas sensing mechanism in these materials is governed by the reactions which occur at the sensor surface between the thin film sensitive layer and the target gas molecules. It involves chemisorption of oxygen on the oxide surface followed by charge transfer during the reactions of oxygen with target gas molecules [65]. The adsorbed gas atoms inject electrons into or extract electrons from the semiconducting material, depending on whether they are reducing or oxidizing agents, respectively [66]. This mechanism results in a change of the film conductivity, which corresponds to the gas concentration. Although semiconductor metal oxide gas sensors are promising, low selectivity, high power consumption and lack of long term stability have prevented their use in more demanding applications [67]. In the literature, there are several approaches to reduce these limitations, such as use of catalysts and promoters, multi-sensor array systems, optimization of sensors’ operating temperature and using materials in nanostructured forms.

The performance of MOS gas sensors improves with a reduction in the size of the oxide particles [10], as the entire thickness of the sensitive layer can be affected by the redox
reaction during the interaction process. As a result, the performance of a gas sensor is directly related to granularity, porosity and ratio of exposed surface area to volume. Recent advances in the synthesis, structural characterization and investigation of physical properties of nanostructured metal oxides provide the opportunity to greatly improve the response of these materials based sensors for gas sensing. A detailed explanation of the gas sensing mechanisms and current status of nanostructured semiconducting metal oxide gas sensors is given in Chapter 2.

Solid-State Semiconductor Gas Sensors

Sensors that fall under this category encompass field effect transistors (FET's), Schottky diodes, and capacitors. Gas sensitive devices based on field effect transistors are generally called GASFETs or suspended gate SGFETs. The specific name of the sensor in the literature denotes the gate material and/or the set-up. These types of sensors consist of a thin catalytic metal layer (platinum or palladium) deposited on top of an insulating oxide layer such as SiO$_2$ and in some cases silicon (Si) or silicon carbide (SiC) substrates. The manufacturing process and packaging technology are similar to standard integrated circuits. The sensors are small, measuring less than 1x1 mm$^2$.

The working principle of these type sensors is based on the reactions between the target gas molecules and the catalytic surface. The reaction products and intermediary products may polarise and adsorb at the metal surface or spill over to the uncovered parts of the insulator surface. For example, hydrogen atoms, formed by reactions of hydrogen or hydrogen-containing species, diffuse through the catalytic metal and form dipoles at the metal-insulator interface [68]. The polarised species at the insulator surface and polarised hydrogen atoms at the metal-insulator interface are in equilibrium with the concentration in the gas phase. They form a dipole layer, which adds to the electric field between the metal and semiconductor, altering the voltage between the gate and the source electrode. This causes a shift in the current-voltage characteristics of the device. In practice, the gas response is measured as the change in the externally applied gate voltage which is required to keep the current through the device constant.

Optimisation of sensor performance to different gases can be achieved by: changing the operating temperature, as the dehydrogenation and the catalytic process is temperature dependent; the metal on the catalytic surface; and the thickness and morphology of the gate metal [69]. These sensors can thus be made sensitive to a broad range of hydrogen-containing or polar compounds. They are stable and exhibit a relatively low sensitivity to humidity.
**Conducting Polymer (CP) Based Sensors**

Polymer gas sensors based on measuring resistance changes in thin film structures have been extensively studied. Among the family of conducting polymers, polyaniline and polypyrrole are possibly the most studied polymers for sensing applications due to their simple synthesis, environmental stability and straightforward non-redox acid doping/base dedoping process to control conductivity [14]. For sensing applications, the suitable polymers have to have a conjugated $\pi$–electron system along the polymer backbone. However, the choice of the polymer is limited to intrinsically conducting polymers (ICP) or those which can be made conducting by doping the polymer with counter ions using reducing (n-doping) or oxidising (p-doping) processes. Conducting polymer layers can be incorporated in many different types of transducers, including conductometric, SAW and optical transducers [70].

Usually a thin polymer film is directly deposited onto the sensor substrate by electrochemical or chemical polymerisation. Drop casting, dip and spin coating, screen printing, layer by layer self assembly and Langmuir-Blodgett techniques can also be used to deposit thin films onto the substrates [71].

Conducting polymer sensors operate at room temperature as opposed to the MOS sensors described previously. Their advantages also include high sensitivity, small size, low production costs and ease of deposition on a wide variety of substrates [72]. Disadvantages include the reproducibility of fabrication (poor batch-to-batch reproducibility), strong humidity interference, and base line drift over time due to oxidation processes or changes in the conformation by exposure to inappropriate compounds.

The sensitivity of these type sensors can be altered over a wide range by incorporating functional side groups to the polymer backbone, the selection of doping ions, the variation of the polymer chain length, condition of the polymerisation and the use of nanostructured forms [72]. Among these options, the nanostructured forms of polymer appear to be the most promising to develop highly sensitive and stable gas sensors. A detailed explanation of the gas sensing mechanisms and current status of nanostructured polymer based gas sensors is given in Chapter 2.

### 1.3 Objectives

In the previous section, the author presented different types of sensors and their gas sensing mechanisms. From this, it is understood that generally MOS material-based sensors operate at elevated temperatures and polymer-based sensors operate at room temperature. It is also
understood that nanostructured materials have high surface to volume ratios, which is a fundamental requirement for gas sensing. Nanostructured material based sensors have the potential to improve sensitivity and stability compared to conventional gas sensors. With that in mind, this research has the following objectives:

- To synthesize nanostructured forms of ZnO and develop novel ZnO nanobelt and nanorod based SAW and conductometric gas sensors to detect H\textsubscript{2}, NO\textsubscript{2} and hydrocarbon gases. The sensor performances (sensitivity, stability and repeatability) will be investigated to optimize operating conditions.

- To synthesize TiO\textsubscript{2} nanoparticles and gold doped TiO\textsubscript{2} nanoparticles for developing novel nanoparticle based SAW gas sensors. Sensitivity and operational temperature will be investigated depending on the doping effect of gold nanoparticles onto the TiO\textsubscript{2} film.

- To synthesize polyaniline nanofibers and develop novel conductometric and SAW sensors based on these nanofibers. Detailed study of sensor performances based on doping, dedoping and variation of doping acids will be performed.

- To synthesize novel nanocomposites containing polyaniline nanofibers and metal oxide nanoparticles and develop novel SAW sensors based on these nanocomposites. The sensor performances will be investigated and compared for room temperature operation.

- Structural characterization of these novel nanostructured materials will be examined to reveal morphology, dimensions and orientation of the materials.

- To explain the gas sensing mechanism of all of the above novel devices.

To develop novel layered nanostructured material/SAW sensors, the author has chosen 64° YX LiNbO\textsubscript{3} and 36° YX LiTaO\textsubscript{3} substrates, as these piezoelectric materials have high electromechanical coupling co-efficients. The SAW devices will employ an intermediate ZnO layer and a sensitive nanomaterial layer. The intermediate ZnO layer was used to protect the IDTs being short circuited when polyaniline nanofiber and polyaniline/metal oxide nanocomposite materials were used as a sensitive layer. It is also used as a seed layer for subsequent growth of nanorods for ZnO nanorod sensor. To develop nanomaterial based conductometric sensors, the author has chosen sapphire substrates with patterned platinum (Pt) IDTs. The thin film of nanostructured materials will be characterized using techniques such as SEM, TEM, XRD, etc.
1.4 Outcomes and Author’s Achievements

This PhD research program has resulted in a number of significant contributions to the field of nanostructured material based SAW and conductometric gas sensors. To the best of the author’s knowledge there have been no literature reports published in the public domain on ZnO nanobelts and nanorods, polyaniline nanofibers and polyaniline/metal oxide nanocomposites based SAW structure for gas sensing applications. The author is the first to propose them.

Thermal evaporation and radio frequency (RF) sputtering methods were used to synthesize and deposit ZnO nanobelts whereas ZnO nanorods were fabricated using a hydrothermal method. Polyaniline nanofibers and its nanocomposites with metal oxides were synthesized with rapidly mixed reaction method.

Nanostructural characterizations provided a powerful platform where important information was extracted to link the material nanostructural morphology to their gas sensing characteristics. Structural characterization techniques revealed that the developed thin films have single crystal, one-dimensional nanostructures.

The major outcomes of this research program can be summarized below:

- Thermally evaporated single crystal ZnO nanobelts with the typical thickness and width-to-thickness ratios in the range of 10 to 30 nm and ~5 to 10, respectively, have been synthesized. Using these nanobelts, layered ZnO/64° YX LiNbO₃ and ZnO/36° YX LiTaO₃ based SAW structures for gas sensing applications were successfully fabricated for the first time and presented in this thesis.

- RF sputtered single crystal hexagonal structure of ZnO nanobelts with average thickness and width of about 10 nm and 50 nm, respectively, have been synthesized. RF sputtered ZnO nanobelt based conductometric devices were successfully fabricated for the first time for gas sensing applications and presented in this thesis.

- Hydrothermally grown ZnO nanorods with the diameters of around 100 and 40 nm on LiNbO₃ and Au (metallization for electrodes), respectively, were successfully fabricated on a layered ZnO/64° YX LiNbO₃ based SAW structure. To the author’s best knowledge, the developed nanomaterials/SAW device is investigated for gas sensing applications for the first time and presented in this thesis.
Hydrochloric acid (HCl) and camphor sulfonic acid (CSA) doped polyaniline nanofibers with average diameter of 30 and 50 nm, respectively, were synthesized using the rapidly mixed reaction method. Polyaniline nanofiber based layered ZnO/64° YX LiNbO₃ structures were then developed for gas sensing applications and to the author’s best knowledge, for the first time nanofibers diameters have been linked to hydrogen gas responses.

Polyaniline nanofiber based conductometric sapphire structures were also fabricated to establish whether SAW response is due to mass or conductivity change. In addition, to the author’s best knowledge, for the first time comparison between doped and dedoped nanofiber sensors responses have been investigated.

Novel polyaniline nanofiber and metal oxide (In₂O₃, WO₃, and SnO₂) nanoparticle composites based ZnO/64° YX LiNbO₃ structures were fabricated and gas sensing results were presented in this thesis.

Highly porous TiO₂ film and Au nanoparticles doped TiO₂ film based 64° YX LiNbO₃ structures have been fabricated. Effects of Au nanoparticles doping on the sensitivity and operating temperatures were obtained and presented in this thesis.

ZnO nanorod based SAW sensor outperformed ZnO nanobelt based sensor in terms of sensitivity, response and recovery times.

CSA doped polyaniline nanofiber based sensors outperformed HCl doped sensors but the latter has faster response.

Doped polyaniline nanofibers based sensors have higher sensitivity than dedoped.

Gold nanoparticle catalyst has improved the sensitivity of TiO₂ based SAW sensor.

The author successfully fulfilled these research objectives by developing highly sensitive nanostructured material based SAW and conductometric devices for gas sensing applications, under room and high temperature operations. From these accomplishments there have been several key outcomes, the results of which have been published in referred journals and presented at international conferences. These include:


13 publications in international conference proceedings.
The author’s work has been presented both personally and on his behalf at several international conferences with the author being fortunate enough to attend the following:


1.5 Thesis Organisation

The remainder of this thesis is primarily devoted to the investigation of nanostructured semiconducting metal oxide and conducting polymer thin films for gas sensing applications and is divided as follows:

- Chapter 2 presents the gas sensing mechanism of semiconducting metal oxides and polymer materials and a literature review on nanostructured ZnO, TiO$_2$, polyaniline and polyaniline/metal oxide composite films for gas sensing. In this chapter it will be shown that nanostructure material based sensors are better than conventional polycrystalline material based sensor for sensing applications.

- Chapter 3 addresses in detail on SAW transducers and the theory behind this type of device response.

- Chapter 4 describes SAW and conductometric transducer designs and outlines the fabrication methods employed to develop the transducers used in this research.

- Chapter 5 describes nanostructured material synthesis and thin film fabrication techniques with particular emphasis on thermal evaporation, RF sputtering, hydrothermal methods, chemical and electrochemical polymerization approaches.

- Chapter 6 describes the instruments (SEM, TEM, XRD etc) used in this study. Without these instruments, the advances towards nanotechnological evolution would not be possible. Chapter six also presents the results obtained from the nanostructural characterization of the ZnO nanobelts and nanorods, TiO$_2$ nanoparticles, polyaniline nanofibers and polyaniline/metal oxide nanocomposites thin films.
Chapter 7 focuses on the gas sensing performance of the developed nanostructured material based sensors. Comparative study of the different nanomaterial/SAW sensors will be discussed. This chapter also describes the four channel computer control gas calibration system used to test the novel gas sensors.

Finally, Chapter 8 presents the conclusions and suggests possible future work.
REFERENCES


Chapter 2

Gas Sensing Fundamentals and Literature Review

2.1 Introduction

The previous chapter outlined the motivation, objectives and outcomes of this research, as well as presented some fundamental aspects of nanotechnology, nanostructured materials and nanotechnology enabled gas sensors. Additionally, readers were also familiarised with fundamental concepts regarding gas sensors and different gas sensing platforms. The purpose of this chapter is to illustrate the gas sensing mechanisms of semiconducting metal oxides and conducting polymer based sensors with a critical literature review on gas sensors based on nanostructured forms of these materials.

Various transitional metal oxides are used as MOS gas sensing materials; however this thesis focuses on ZnO and TiO$_2$ in their nanostructured forms. Both ZnO and TiO$_2$ films have been investigated as sensors for H$_2$, NO$_2$, CO, O$_2$ and hydrocarbons gases.
Out of all conducting polymers, polyaniline and polypyrrole are probably the most extensively investigated for gas sensing; however this thesis focuses only on polyaniline in the nanofiber form. Polyaniline is unique among the family of conducting polymers in that its conductivity can reversibly be controlled by the protonation of the imine sites and the oxidation of the main polymer chain [1].

It is well known that MOS sensors require an elevated temperature (200-600°C) for optimum operation [2-3]. However, in some cases room temperature operation of a sensor is highly desirable to extend sensor life time and reduce power consumption. Although, polyaniline based sensors operate at room temperature, it is not as sensitive as metal oxides towards gas species. Thus, there is a growing interest to combine both organic and inorganic materials for gas sensing applications. To explore this novel idea, this chapter also included a critical literature review on polymer and metal oxide nanocomposites based gas sensors.

### 2.2 Current Status of Nanostructured Material Based Gas Sensors

Nanostructured materials - materials having at least one dimension between 1 and 100 nm, have received growing interest for gas sensing applications. These materials can be classified into different categories depending on the number of dimensions that are nanosized such as zero dimensional (quantum dots), one-dimensional (nanowires, nanobelts) and two dimensional (films). Of these, one dimensional (1D) nanostructures such as wires, rods, belts, tubes, and fibres are the main focus of intensive research for nanoscale device applications [4].

Studies on novel physical properties and phenomena, and potential applications of nanomaterials are possible only when nanostructured materials are made available with the desired size, morphology, crystal structure and orientation, and chemical composition. Thus, synthesis and processing of nanomaterials are the first and essential aspect in nanotechnology. Different techniques have been adopted to synthesize and fabricate 1D nanostructures on substrates. However, a terminology for these peculiar 1D nanostructures has not been well established and a variety of names appear in the literature. For example, the structure of nanowires, nanofibers and nanorods is similar having a wide range of diameters (less than 100 nm) and lengths. The typical length of the nanowires and nanofibers ranges from several micrometers to a few hundred micrometers, whereas the length of nanorods is limited to a few micrometers. Nanotubes possess wire-like nanostructures with
hollow cores. Nanobelts are found to have a uniform rectangular cross-section along their length, and widths typically range from several tens to several hundred nanometers [5]. A detail review of these 1D nanostructured materials for gas sensing applications will be given below.

2.2.1 Review on Nanostructured Metal Oxide Sensors

2.2.1.1 Nanostructured ZnO Sensors

One dimensional ZnO nanorods, nanobelts and nanowires based gas sensors have been studied by a number of researchers [6-19]. Kang et al. [6] developed ZnO nanorod based H₂ and O₃ sensors by molecular beam epitaxy. They found that the developed sensors were sensitive to H₂ at 112°C and towards O₃ at room temperature. Wang et al. [7, 8] developed ZnO nanorods using molecular beam epitaxy (MBE) for H₂ sensing. They found that sputter-deposited Pd or Pt on the nanorod surface increased the sensor sensitivity by a factor of 5 and the sensor could detect down to 10 ppm H₂ at 25°C. Xu et al. [9] developed a hydrothermally prepared ZnO nanorod based gas sensor and found that the sensor has relatively high sensitivity and stability. Gao et al. [10] developed multipod and tetrapod-shaped ZnO nanorod gas sensors for ethanol detection and found that multipod-shaped nanorods had higher sensitivity than tetra-pod-shaped nanorods.

Zhang et al. [11] developed ZnO nanorod and nanowire based humidity sensors by the vapor-phase transport method. They found that at room temperature the sensors have high sensitivity, good long-term stability, and fast response. Wang et al. [12] developed a hydrothermally grown ZnO nanorod based sensor to detect H₂S and found that the sensor was able to detect H₂S at ppb levels at room temperature. Rout et al. [13] have employed ZnO nanorods, nanowires and nanotubes to detect H₂ and ethanol. They found high sensitivity at 200°C and even reduced the optimum operating temperature to 150°C after impregnation with 1% Pt.

Xiangfeng et al. [14] developed a ZnO nano-tetrapod based sensor to detect ethanol and methane and achieved high sensitivity at 300°C. Baratto et al. [15] developed nanostructured fibers of ZnO to detect NO₂ down to 0.4 ppm at 100°C. Wan et al. [16] studied the ethanol sensing characteristics of a ZnO nanowire sensor fabricated with the MEMS technology. It was found that the sensor had a high sensitivity to 200 ppm ethanol at 300°C. The same group also fabricated individual ZnO nanowire FET type sensors [17] which exhibited high sensitivity to oxygen by changing the source drain current and shifting the threshold voltage.
A ZnO nanowire field-effect chemical sensor and their sensing properties for NO$_2$ and NH$_3$ were presented by Fan et al. [18]. They observed that the gate potential could affect the detection sensitivity, and the adsorbed gas molecules could be electrically desorbed by applying a large negative gate voltage. Wang et al. [19] studied ZnO nanowire based quartz crystal microbalance device for NH$_3$ sensing at room temperature. The ZnO nanowires showed high sensitivity to ammonia in the range of 40–1000 ppm. The response was as fast as 5 sec over the concentration range 40–1000 ppm. Meanwhile, they found that the response varied with the thickness of the ZnO nanowires layer.

2.2.1.2 Nanostructured SnO$_2$ Sensors

A conductometric tin oxide nanobelt based gas sensor was first reported by Comini et al [20]. They synthesized SnO$_2$ nanobelts by a thermal evaporation method and then deposited on alumina substrates for CO, NO$_2$ and ethanol sensing. They found that the nanobelt sensors could sense as low as 30 ppm CO, 200 ppb NO$_2$ and 10 ppm ethanol at 350°C. Recently, Liu et al. [21] reported a single square shaped SnO$_2$ nanotube ethanol gas sensor which was bridged between two interdigitated Pt electrodes. They reported that the advantages of using nanotube sensors included the dramatically accelerated transport of gas in and out of the box beams, significantly increased active surface to volume ratios and increased flexibility in surface modification for chemically or biologically selective catalysis, drastically enhanced carrier mobility due to shorter diffusion lengths, radically increased population of defects at surfaces/interfaces for fast electrode kinetics, and quantum interactions at the nanoscale.

Wang et al. [22] developed a SnO$_2$ nanobelt based field-effect transistor to detect oxygen. They have also assembled SnO$_2$ nanobelts with a low-power micro-heater for detecting dimethyl methyl-phosphonate, a nerve agent stimulant [23]. A focused ion beam method was used to deposit a thin Pt coating on the contact location between the nanobelt and each Pt electrode so as to improve the electrical contact. Yang et al. [24] reported a room temperature photochemical NO$_2$ sensor based on individual single-crystalline SnO$_2$ nanoribbons. They also [25] found that SnO$_2$ nanoribbons with exposed (101) and (0 1 0) surfaces were highly effective NO$_2$ sensors at room temperature and can sense as low as 5–10 ppm of NO$_2$.

Kolmakov et al. [26] investigated the gas sensing properties of individual SnO$_2$ nanobelts before and after functionalization with Pd catalyst particles. The Pd-functionalized nanostructures exhibited a dramatic improvement in sensitivity towards oxygen and hydrogen due to the enhanced catalytic dissociation of the molecular adsorbate on the Pd nanoparticle surfaces and the subsequent diffusion of the resultant atomic species to the oxide surface. Faglia et al. [27] presented that the visible photoluminescence (PL) of SnO$_2$
nanobelts could be quenched by nitrogen dioxide at a ppm level in a fast (time scale order of seconds) and reversible way.

Moskovits et al [28] reported the O₂ and CO sensing properties of an individual SnO₂ nanowire. Their experimental observations concluded [29] that the chemical reactivity and selectivity of nanowire’s surface is affected by the electron density states inside the nanowire and the electron exchange between the surface states and the bulk takes place within a surface layer whose thickness is of the order of the Debye length, λ₀. Xia et al. [30] prepared a polycrystalline SnO₂ nanowires film for gas sensing applications. The nanowire sensor exhibited high sensitivity and reversibility when exposed to ethanol vapour (V<sub>ethanol</sub>/V<sub>air</sub> ~6%), 20 ppm CO, and 500 ppm H₂. The authors suggested that this could be attributed to the intrinsically small grain size and high surface-to-volume ratios associated with the polycrystalline nanowires. The nanosized SnO₂ grains in the nanowires allowed the sensors to be operated in the most sensitive, grain-controlled mode.

Wan et al. [31] developed Sb-doped SnO₂ nanowire based gas sensor for ethanol sensing. They found that the sensor is sensitive to a wide range of ethanol concentrations (10–1000 ppm) at 300°C with a fast response and recovery of 1 and 5 s, respectively. Ramgir et al [32] reported Ru-doped SnO₂ nanowires for NO₂ and LPG sensing. The nanowires exhibited a highly selective sensing behaviour towards NO₂ at room temperature.

2.2.1.3 Nanostructured TiO₂ Sensors

Grimes et al. [33–36] reported several promising results on TiO₂ nanotube based sensors for H₂ sensing. Most recently they developed a room temperature hydrogen sensor comprised of a TiO₂ nanotube array which can recover substantially from poisoning by environmental contamination [33]. The nanotube arrays are fabricated by anodizing titanium foil in an aqueous electrolyte solution containing hydrofluoric acid and acetic acid. A 10 nm coating of Pd was evaporated onto the surface of the titania nanotube array film to enhance the hydrogen sensitivity of the sensor, which showed over a 4 order of magnitude change in electrical resistance upon exposure to 100 ppm hydrogen at 25°C.

2.2.1.4 Nanostructured MoO₃ Sensors

In 2005, Comini et al. [2] developed MoO₃ nanorod based conductometric alumina gas sensors. They investigated the sensor responses towards CO and ethanol at different temperatures and compared the nanorod based sensor response to the conventional MoO₃ thin film sensors. They found the nanorod based sensor is 10 times more sensitive than the conventional one. The authors ascribed the improved performances to the high surface to
volume ratios of the materials due to the intrinsic morphology of nanorods and to the nanosized lateral dimensions.

### 2.2.1.5 Nanostructured In$_2$O$_3$ Sensors

Li et al [37-38] have reported a series of novel works on In$_2$O$_3$ nanowire based gas sensors. They developed a single In$_2$O$_3$ nanowire based field effect transistor (FET) to work as a chemical sensor for NO$_2$ and NH$_3$ at room temperature. The sensor showed responses ($R_{\text{gas}}/R_{\text{argon}}$) as high as $10^6$ for NO$_2$ and $10^5$ for NH$_3$. The response time was determined to be 5 s for 100 ppm NO$_2$ and 10 s for 1% NH$_3$, and the lowest detectable concentrations were 0.5 ppm for NO$_2$ and 0.02% for NH$_3$. Additionally, a change of conductance in opposite directions was observed with different nanowire sensors and the authors suggest that this response anomaly is caused by various doping concentrations in the In$_2$O$_3$ nanowires, pointing out that strict control in the deposition process and post treatment procedures is necessary to produce reliable sensors.

Zhang et al [39] demonstrated room temperature detection of NO$_2$ down to ppb levels using transistors based on both single and multiple In$_2$O$_3$ nanowires. The multi-wire sensor showed an even lower detection limit of 5 ppb, compared to the 20 ppb limit of single nanowire sensors. This room temperature detection limit is the lowest level so far achieved with all metal oxide film or nanowire sensors. The authors observed a selective response towards NO$_2$ using the multiple nanowire-based sensor and suggested an "ensemble-averaging effect" as one of possible reasons for the observed high selectivity. On the basis of their previous study, they suggested that, accordingly, a large ensemble of In$_2$O$_3$ nanowires, with an appropriate doping level distribution, could have two opposite sensing responses, cancelling out each other, and resulting in the immunity to NH$_3$. This unique property of In$_2$O$_3$ nanowires offers a new way to achieve selectivity.

Chu et al [40] investigated an In$_2$O$_3$ nanowire based conductometric sensor towards ethanol vapour. A mixture of In$_2$O$_3$ nanowire and polyvinyl alcohol solution was coated on alumina tubes with two gold contacts at the end. The results revealed that the sensors exhibited higher response and good selectivity to C$_2$H$_5$OH at 370°C. The response time was about 10 s and recovery time was shorter than 20 s.

### 2.2.1.6 Nanostructured WO$_3$ Sensors

A tungsten oxide nanowire based NO$_2$ gas sensor and its sensing properties was first reported by Sawicka et al. [41] in 2005. The nanowires were synthesized by electro-spinning and the effect of processing parameters variation on the sensitivity was studied. A comparison of
nanowire based sensor response to sol-gel prepared WO$_3$ thin films response was also presented. The nanowire based sensor showed better NO$_2$ gas sensing performances compared to sol-gel processed conventional films. They ascribed these results to the larger surface area of the nanowires. Kim et al. [42] studied a gas sensor based on a non-stoichiometric tungsten oxide nanorod film. The sensor was fabricated on Si substrates by using MEMS and silicon technology. The authors measured the sensor responses to 2% N$_2$ (or air), 1000 ppm ethanol, 10 ppm NH$_3$, and 3 ppm NO$_2$ in both dry air and nitrogen atmosphere at room temperature.

### 2.2.2 Review on Nanostructured Polymer Sensors

#### 2.2.2.1 Polyaniline Nanofiber Sensors

Polyaniline nanofibers, with diameters in the 30-100 nanometer range, possess much larger surface areas per unit mass and permit easier addition of surface functionality and interaction compared with traditional polyaniline which is highly agglomerated and poorly dispersible in water. The structure of traditional polyaniline requires dissolving in a solvent such as N-methyl pyrrolidinone (NMP) and casting into a dense film. Polyaniline nanofibers have a cylindrical morphology and form porous structures when deposited as thin films. Therefore, the nanofiber based thin films have higher surface to volume ratios than traditional thin films of the same thickness [43]. The three-dimensional porous structure of a polyaniline nanofiber film allows easy diffusion of gas molecules in and out of the film and the nano-scale fiber diameters lead to rapid diffusion of gas molecules into the polyaniline as shown in Figure 2.1. As a result, most literature reports on polyaniline nanofibers [44-49] indicate that nanostructured polyaniline outperforms conventional polyaniline for gas sensing applications.

![Schematic diagram of a traditional polyaniline thin film (left) and nanofibers (right) exposed to gas molecules (arrows) [45].](image-url)
The sensitivity of conventional polyaniline thin film gas sensors depends on the film thickness [45]. Generally, sensor sensitivity increases with a reduction of film thickness as the entire thickness of the film is affected by the reactions with gas species in a short period of time [47]. On the other hand, sensitivity of a polyaniline nanofiber sensor is independent on film thickness in the range of 0.2-2 µm, due to the porous structure of the film which leads to the predominance of surface phenomena over the bulk material response [45]. Therefore, even in thicker films, all the fibers can contribute to the sensing process as shown in Figure 2.2. This advantage allows the fabrication of sensors with reproducible responses that have a large tolerance in thickness variation [45].

![Figure 2.2: Schematic diagram of polyaniline nanofiber based films with different thickness [45].](image)

Virji et al. [44-46] developed polyaniline nanofiber thin film sensors and compared them to conventional polyaniline sensors. They presented five different gas sensing results with response mechanisms including acid doping (HCl), base dedoping (NH₃), reduction (N₂H₄), swelling (with CHCl₃), and polymer chain conformational changes (induced by CH₃OH). In all cases, the polyaniline nanofibers performed better than conventional thin films. Aussawasathien et al. [49] developed polymer nanofiber based sensors using electro-spinning and compared them with thin film counterparts. They achieved significantly enhanced sensitivity with the nanofiber sensors for humidity measurements as well as for H₂O₂ and glucose concentration measurements. Liu et al. [50] developed polyaniline nanowire based chemical sensors to detect NH₃ gas. They found that the response time of nanowire based sensors with various diameters corresponds to the radius-dependent diffusion time of ammonia gas into the wires.
Liu et al. [51] found that oriented polyaniline nanowire based sensors are highly sensitive towards \( \text{H}_2\text{O}_2 \), which has great importance for bio-sensing based on oxidase type enzymes. Li et al. [52] suggested that thin films of polyaniline synthesized electrochemically can outperform chemically synthesized nanofibers for neutral gas sensing such as water or methanol vapor. Misra et al. [53] developed vacuum-deposited nanocrystalline polyaniline thin films for carbon monoxide detection and observed high sensitivity, and a fast response (10 s) towards CO. Wang et al. [54] developed a conductometric sensor using arrays of polyaniline nano-framework junctions for both gas and liquid phase detection. They observed repeatable and reversible responses towards HCl, \( \text{NH}_3 \) and ethanol vapour.

### 2.2.3 Review on Polymer/Semiconducting Metal Oxide Nanocomposites Gas Sensors

There is a growing interest to combine both organic and inorganic materials for applications in electronics and optics [55]. The combination of nanosized metal oxides and polyaniline has the potential to increase the sensitivity of the conducting polymer. Such composites can operate at room temperature and the sensitivity towards different gas species can be optimised by the volume ratio of nanosized metal oxides. In addition, the composite may have better long term stability. The nanocomposite organic/inorganic materials are considered as bi-phase materials where the organic and inorganic phases are mixed at the nanometer scale. The properties of nanocomposite materials depend not only on the properties of their constituents but also on their combined morphology and interfacial characteristics [56].

A number of researchers have already developed polyaniline/inorganic nanocomposite sensors. Conn et al. [57] developed a polyaniline/PtO\(_2\) based selective \( \text{H}_2 \) sensor and reported that the conductivity of polyaniline increases with \( \text{H}_2 \) exposure, due to the formation of water. It is known that water present in the polymer takes part in charge transfer leading to an increase in the conductivity of polyaniline which is reversible [58-59]. Wang et al. [60] developed polyaniline intercalated MoO\(_3\) thin film sensors and reported that the conductivity change is due to the reversible absorption of analyte. Parvatikar et al. [61] developed polyaniline/\( \text{WO}_3\) composite based sensors and reported that conductivity of the film increases with increasing humidity. Ram et al. [62] developed conducting polymer/\( \text{SnO}_2\) and \( \text{TiO}_2\) nanocomposite thin film based sensors and found that conductivity of the film increases with \( \text{NO}_2 \) exposure. Geng et al. [63] synthesized polyaniline/\( \text{SnO}_2\) hybrid materials by a hydrothermal process for gas sensing applications. They found that hybrid materials are sensitive to ethanol and acetone vapor at 60 to 90°C.
2.3 Gas Sensing Mechanism of MOS Sensors

Binary n-type semiconductor oxides such as tin oxide (SnO$_2$), titanium dioxide (TiO$_2$) and indium oxide (In$_2$O$_3$) have been extensively investigated as gas sensing materials since Seiyama first observed gas sensing properties of ZnO [64]. The gas sensing mechanism in these material based devices is governed by the reactions which occur at the surface of the metal oxide with the gas molecules. It involves chemisorption of oxygen on the oxide surface followed by charge transfer during the reaction of chemisorbed oxygen with target gas molecules [65]. The adsorbed gas atoms inject electrons into or extract electrons from the metal oxide, depending on whether they are reducing or oxidizing agents, respectively [66]. Thus, small amounts (down to ppb) of a gaseous species present in air can be detected by metal oxide sensors from a change in electrical resistance.

It is well known that in air, oxygen molecules adsorb onto the surface of the MOS layer to form O$_2^-$, O$^-$ and O$_2^+$ ions by extracting electrons from the conduction band depending on the temperature [65, 67]. The positively charged MOS surface and negatively charged adsorbed oxygen ions form a depletion region at the surface. At elevated temperatures, the interaction of the target gaseous molecules with the adsorbed oxygen will change the depletion layer or the barrier height of the metal oxide grains, particles or nanostructures. These changes are transduced into an electrical output signal depending on the transducing platforms. The porosity of the film, the grain size (nanostructured forms) and the different grain/nanostructure intersections will determine the output signal, which takes into account the whole sensitive layer. Gas sensing mechanisms and models proposed by Moseley [68,69], Morrison [66, 70], Gopel [71-72], Schierbaum [73], Yamazoe [74] and Weimar [75] will be employed to gain fundamental understanding of MOS sensing mechanisms in nanostructures and included at the end of this Chapter. All are well known researchers in the field of MOS gas sensors and have provided the foundations to contemporary theories of MOS gas sensing principles. The chemistry of metal oxide and gas molecule interactions is same for both polycrystalline and nanostructured materials based sensors. Thus, to some extent, the conventional gas sensing theories still apply to the nanostructured MOS based sensors. However, in nanostructured sensors, the gas sensing mechanism will be influenced by quantum effects and crystallinity. In this thesis, the author has started with the gas sensing mechanism of traditional polycrystalline thin film MOS gas sensors and extended the work with an example of nanostructured material based sensors.

Sensors based on metal oxide films are mature and the effects of its sensitive layer morphology, such as grain size, structural formation, surface to volume ratio and film thickness on sensitivity are well recognized [20]. Traditional thick-film based gas sensors
operate on the basis of both surface and bulk conductivity changes. The sensitivity of this type of sensor is poor as gas molecules can not penetrate and interact with the whole bulk of the film in a short period of time. Thus dynamic performances of this type of sensor are also poor. In thin film gas sensors, response is primarily based on surface conductivity changes; hence, gas molecules need not diffuse deeply within the layer. As a result, thin film gas sensors achieve improved dynamic performances. Additionally, thin film gas sensors based on nanostructured metal oxides which have high surface to volume ratios will have increased sensitivity. Moreover, if the thin film is porous (usually nanowires, nanorods, nanofibers based films show porosity) the whole depth of the sensitive thin film can be affected by interactions with the gas species, rather than only the surface.

Long term stability of conventional polycrystalline thin film sensors is poor due to gradual deformation of polycrystalline films at high temperature operations. The author believes long term stability of the MOS sensors could be improved using single crystal nanostructured films as these are less susceptible to crystallographic deformation. Hereafter, attention will be focused on the role of oxygen surface species on the sensitive film and the gas sensing mechanisms.

2.3.1 Oxygen Response Mechanism: Adsorption Model

The conductivity of a metal oxide film can be altered by modulating the conductance of the materials. The bulk and surface conductivity changes in a MOS film are predominantly dependant on the partial pressure of atmospheric oxygen. Thus, at elevated temperatures, the stoichiometry of semiconducting oxides changes as a function of the ambient oxygen. Most of the MOS gas sensors operate by adsorption of ambient oxygen, leading to a high resistance for n-type metal oxides and a lower resistance for p-type metal oxides. The change in stoichiometry affects the electrical conductivity of the materials, \( \sigma \), which can be expressed by the following equation [68],

\[
\sigma = \sigma_o \exp\left(-\frac{E_a}{kT}\right) p(O_2)^{1/n},
\]

where \( k \) denotes Boltzmann’s constant, \( T \) is the temperature (°K), \( E_a \) is the activation energy of conduction and \( p(O_2) \) is the partial pressure of the gaseous oxygen. The activation energy is the sum of the energy required to form the ionic defects and the subsequent ionization to form charge carriers in the conduction or valence band. The sign and value of \( n \) (see Eq. 2.1) depend on the nature of the point defects arising when oxygen is removed from the lattice.
To illustrate defect chemistry of the metal oxides at high temperature, the following example (TiO$_2$) is given. When oxygen sensors based on TiO$_2$ are exposed to low pressure gaseous oxygen at temperatures high enough to create defects, reduction of TiO$_2$ is believed to occur resulting in the formulation of Ti interstitials ($T_i^{***}$). The reaction is given by [68):

$$Ti_i^{**} + 2O_{o}^{*} \Rightarrow Ti_i^{****} + 4e^- + O_2 \text{ (gas)}$$

(2.2)

with the charge neutrality,

$$4 \cdot [T_i^{****}] = n$$

(2.3)

The equilibrium constant of the reduction reaction (2.2) is

$$K_R = [T_i^{****}] \cdot n^4 \cdot p(O_2)$$

(2.4)

When equation (2.3) and (2.4) are combined,

$$n = 4 \cdot [T_i^{****}] = (4K_R)^{1/7} \cdot p(O_2)^{-1/7}$$

(2.5)

The reduction of TiO$_2$ by formulation of Ti interstitial defects has a dependence on oxygen pressure of $n = -5$. Thus, the conductivity of this type oxygen sensor depends on temperature as well as $p(O_2)$, as defect chemical equilibrium constants are exponentially dependent on temperature. The equilibrium between oxygen in the gas phase and lattice oxygen can be useful in designing oxygen gas sensors. However, for sensing other gases most metal oxide sensors rely on surface conduction which will be presented next.

### 2.3.2 Surface Conductance in Semiconducting Oxide Films

Unlike, the mechanism of bulk conductivity changes in semiconducting oxides, surface conductance does not depend heavily on the defect chemistry or oxygen partial pressure of the oxide. Instead, surface conductivity changes occur when a reactive gas changes the equilibrium condition of the surface processes, which are not at equilibrium with the bulk [68]. It is widely accepted that in an air environment, oxygen molecules adsorb onto the surface of the metal oxide layer to form O$_2^-$, O$^-$ and O$^2-$ ions by extracting electrons from the conduction band depending on the temperature [65, 67]. These negatively charged oxygen adsorbates play an important role in detecting gases such as H$_2$ and CO. Takata et al [76] found the stable oxygen ions were O$_2^-$ below 100°C, O$^-$ between 100 and 300°C and O$^2-$ above.
300°C on ZnO surfaces. The oxygen adsorptions on the surface of metal oxides can be explained by the following equations [76]:

\[
\begin{align*}
O_2 \text{(gas)} & \overset{\geq}{\rightarrow} O_2 \text{(ads)} \tag{2.6} \\
O_2 \text{(ads)} + e^{-} & \overset{\geq}{\rightarrow} O_2^{-} \text{(ads)} \tag{2.7} \\
O_2 \text{(ads)} + 2e^{-} & \overset{\geq}{\rightarrow} 2O \text{(ads)} \tag{2.8} \\
O_2^{-} \text{(ads)} + e^{-} & \overset{\geq}{\rightarrow} O^{2-} \text{(ads)} \tag{2.9}
\end{align*}
\]

In the case of n-type semiconducting oxides, the positively charged oxide surface and negatively charged adsorbed oxygen ions form a depletion region at the surface. Thus, the resistance of an n-type semiconducting oxide gas sensor in air is high, due to the development of a potential barrier. A space charge layer is formed due to the electron depletion at the surface by chemisorption. The space charge layer thickness \( \lambda_d \) (also expressed by the Debye length) can be defined using Poisson’s equation as follows [68]:

\[
\lambda_d = \frac{Q_s}{e \cdot N_D} = \left[ \frac{2 \cdot K \cdot \varepsilon_0 \cdot V_s}{e \cdot N_D} \right]^{1/2} \tag{2.10}
\]

where \( Q_s \) is the surface charge density, \( N_D \) is the number of ionized donor states per unit volume, \( e \) is the carrier charge, \( K \) is the static dielectric constant of the oxide, \( \varepsilon_0 \) is the permittivity of the vacuum, and \( V_s \) is the surface potential barrier height. Using typical values of \( K\varepsilon_0 \sim 10^{-12} \, \text{F/cm} \), \( N_D \sim 10^{18} - 10^{20} \, \text{cm}^{-3} \) and \( V_s \sim 1 \, \text{V} \), from Equation 2.10, the space charge layer thickness is around 1 – 100 nm [68].

A schematic of a few grains of porous semiconducting oxide film (large grain at top and small grain at bottom) and the space charge region around the surface of each grain and at inter-grain contacts is shown in Figure 2.3 as an example. The space charge region which is being depleted of electrons is more resistive than the bulk of the materials. The band model for corresponding grain model is also given on the Figure 2.3. The band model shows potential barriers formed at inter-grain contacts and this barrier potential varies with the amount of adsorbed oxygen [70]. It can be seen that the carriers have to overcome a barrier of \( eV_s \) for inter-grain transport. The surface barrier \( V_s \) is a function of temperature and atmospheric oxygen pressure. When an n-type metal oxide surface is exposed to a reducing gas such as \( \text{H}_2 \) or \( \text{CO} \) at elevated temperatures, the oxygen adsorbates are removed by the reduction reaction, so that the steady-state surface coverage of the adsorbates is lowered. Around 300°C, the reactions can be expressed by the following equations [70]:
\[
\begin{align*}
O_{\text{(ads)}} + H_2 &\rightarrow H_2O + e^- \\ (2.11) \\
O_{\text{(ads)}} + C O &\rightarrow C O_2 + e^- \\ (2.12)
\end{align*}
\]

During the reaction process, the electrons trapped by the oxygen adsorbates return to the oxide grains, leading to a decrease in the potential barrier height and drop in resistance. These resistance changes are used as the measurement parameter of the semiconductor gas sensor.

![Diagram of gas sensing layer with geometry and energy band](image)

**Figure 2.3:** Schematic representation of a porous sensing layer with geometry and energy band ($\lambda_D$ Debye length, $X_g$ grain size) [75].

The mean diameter ($X_g$) of grains or crystallites in metal oxides greatly influences gas sensing properties. It has been shown that sensor sensitivity increases with decreasing grain size [77]. The grain size effects of metal oxide polycrystalline materials can be summarised in three
cases assuming a chain of uniform crystallites of size $X_g$ connected each other through necks and grain boundary contacts. These are:

- $X_g >> 2\lambda_D$: grain boundary resistance control;
- $X_g \geq 2\lambda_D$: neck resistance control;
- $X_g << 2\lambda_D$: grain resistance control;

Among the three cases, grain resistance control is the most preferable for gas sensing. In grain resistance control, the grain resistance dominates the resistance of the whole chain and in turn, the film resistance, so that grain structures, morphology or crystallinity are the dominant factors for controlling device sensitivity. Thus, smaller grain sizes would be more sensitive than larger ones [77]. To illustrate the resistance of a nanorod based film, a schematic representation is given in Figure 2.4 where $R_B$, $R_C$ and $R_N$ denote resistance for bulk nanorod, nanorod contact and nanorods neck, respectively. It is perceived that when the nanorod diameter $X_g$ is less than twice of the space charge depth then resistance $R_B$ will be predominant in determining total film resistance. In this condition, the nanorod based thin film sensor will have high sensitivity towards gas species.

![Figure 2.4: Schematic representation of resistance on nanorod boundaries and contacts. (Dark areas refer to the space-charge region)](image)

The particle or grain size of a polycrystalline semiconducting oxide gas sensor is considerably greater than the depth of the surface space charge region, thus, electrical conduction is controlled by the grain boundaries. However, nanostructured materials have greatly reduced size particles, grains, rods, wires, belts whose dimensions are comparable to the depletion layer depth. Under these conditions, oxygen adsorption to the nanostructures will lead to a complete depletion of conduction-band electrons with a large variation in resistance. Thus, in this work, nanostructured materials were chosen to produce highly sensitive gas sensors. A schematic representation of the physical and band models for a nanorod based oxide surface is presented in Figure 2.5. The band model shows potential barriers formed at nanorod
contacts and this barrier potential varies with the amount of adsorbed oxygen. It should be noted that this barrier potential is much higher than conventional inter-grain potential barriers due to a complete depletion of electrons in nanorods. Thus the scale of conductivity modulation in nanostructures is much greater than conventional grains after exposure to gases.

Figure 2.5: Schematic representation of a sensing layer based on nanorods of semiconducting oxide showing inter-rod contact resistance.

Figure 2.6: Schematic diagram of a porous ZnO nanorod based film exposed to gas molecules (arrow).

The morphology of the thin film sensing layer also has an influence on the sensor sensitivity and it can be simply divided into compact and porous ones. First, in compact sensing layers, gases cannot penetrate into the layer and the gas sensing reaction is confined to the surface of
the sensing layer. Second, in the porous layer, gases can access all of the volume of the sensing layer, and the gas sensing reaction can therefore take place at the surface of individual grains/nanostructures, at grain-grain boundaries and interfaces between grains and electrodes. A schematic of ZnO nanorod based films showing inherent porosity is shown in Figure 2.6. Thus, the use of nanostructured metal oxides could greatly improve gas molecule diffusion, since nanostructured metal oxides have much greater exposed surface area, as well as much greater penetration depth for gas molecules, relative to their bulk compact materials.

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

2.4 Gas Sensing Mechanism of Polymer Based Sensors

Conducting polymers have received increasing interest as an alternative to metal oxide semiconductors for gas sensors. This is due to their room temperature operation, low fabrication cost, ease of deposition onto a wide variety of substrates and their rich structural modification chemistry [78-79]. Among the family of conducting polymers, polyaniline is one of the most highly studied materials because of its simple synthesis, environmental stability and straightforward non-redox acid doping/base dedoping process to control conductivity [80-81]. By changing the doping level and morphology, the conductivity of polyaniline can be tuned for specific applications such as sensors, actuators, rechargeable battery electrodes, anticorrosion coatings, gas-separation membranes, display devices and field effect transistors (FETs) [82]. Thus, in this PhD work, the author selected polyaniline from the conducting polymer group to synthesize in their nanostructured form for gas sensing applications.

Polyaniline in the emeraldine oxidation state can be reversibly switched between electrically insulating emeraldine base (Fig. 2.7: top) and conducting emeraldine salt forms (Fig. 2.7: middle and bottom) [83-84]. The conductivity of polyaniline can be varied by 10 orders of magnitude by controlling the degree of imine nitrogen protonation (doping). The doping level can be altered by using variable amounts of a wide variety of protonic acids. The dopants can be removed by a reversible reaction with any strong base such as ammonium hydroxide.
Figure 2.7: Polyaniline in the emeraldine oxidation state can exist in either its undoped (top), intermediate bipolaron (middle) or fully doped acid form (bottom).

The polyemeraldine form consists of amine (-NH-) and imine (=N-) sites in equal proportions. The imine sites are protonated preferentially to achieve an intermediate bipolaron form (Fig. 2.7: middle), which further undergoes dissociation to form a delocalized polaron lattice (Fig. 2.7: bottom) [83]. A polaron can be considered a type of electronic defect that occurs within the π orbitals of the polymer backbone and is the charge carrier responsible for the relatively high conductivity of doped polyaniline [84]. By controlling the pH of the dopant acid solution any desired quantity of dopants can be added until all imine nitrogens are protonated. Dopants can be removed by a reversible reaction with any strong base such as ammonium hydroxide.

The conductivity of polyaniline depends on both the degree of protonic acid doping of the imine sites and the oxidation state of the main polymer chain [85]. Any interaction with polyaniline that alters either of these processes will affect its conductivity. Reduction (n-doping) or oxidation (p-doping) of the conducting polyaniline emeraldine salt by chemical or electrochemical processes change the number of electrons associated with the polyaniline backbone making the polymer to the insulating leucoemeraldine or pernigraniline oxidation states, respectively. As a result, redox active chemicals and gases can affect the conductivity of polyaniline by changing its inherent oxidation state. Neutral, volatile organic compounds are able to change the conductivity of doped polyaniline films through physical effects as a result of polymer swelling, alignment, crystallization, solvation, or by affecting the doping level [86-89]. It was reported that partial electron transfer occurs between the polyaniline
and the volatile organic compound analytes which may increase or reduce the concentration of the charge carriers along the polymer backbone, and hence polymer conductivity [90]. Functional additives incorporated into the polyaniline structural matrix, such as metals, metal oxides, enzymes, etc. can change the electrical characteristics of polyaniline. This versatility has made polyaniline attractive for a broader scope of design and development of highly efficient sensors [91].

Conducting polymer gas sensors based on measuring resistance changes in thin film structures have been studied by a number of researchers. A detailed review of polyaniline and polymer sensors can be found in references [92] and [93], respectively. Roy et al. [94] developed a doped polyaniline based hydrogen sensor using a chemical polymerization method. This structure showed no response to H₂; however, when palladium was dispersed across its surface the conductivity decreased during H₂ exposure. Agbor et al. [95] developed thin films of non-doped polyaniline gas sensors by spin coating, evaporation and using a Langmuir-Blodgett technique. They found that the conductivity of polyaniline is increased by NO₂, SO₂ and H₂S exposure, decreased by N₂ exposure, and remained unaffected by CO and CH₄ exposure. Torsi et al. [96] found that polypyrrole and Cu-doped polypyrrrole sensors showed increased resistance and a Pd doped polypyrrrole sensor showed decreased resistance towards H₂ exposure. Xie et al. [97] reported gas sensors based on an ultra-thin film of acidic polyaniline. They showed that exposing a polystyrenesulfonic acid based polyaniline sensor to the gas NO₂ decreased the film conductivity.

The mechanism for hydrogen sensing is at the moment still unclear. In this PhD work, both SAW and conductometric sensor test results showed that resistance decreases in doped polyaniline on exposure to H₂. The author believes the hydrogen may form a bridge between nitrogen atoms on two adjacent chains or there may be partial protonation of some of the imine nitrogens [98]. MacDiarmid [98] has presented a possible mechanism for the interaction of hydrogen with polyaniline and it is reproduced in Figure 2.8, with A representing any dopant anion. In this scheme, hydrogen interacts with doped polyaniline at the charged amine nitrogen sites. H₂ bond dissociation follows with formation of new N-H bonds to the amine nitrogen of the polyaniline chain. Subsequent charge transfer between adjacent amine nitrogens returns the polyaniline back to its polaronic, doped, emeraldine salt state with a release of hydrogen, making this reaction fully reversible. It has also been suggested that the resistance change is caused by the formation of water [57].

The hydrogen storage properties of conducting polymers have been actively studied. Cho et al. [99] suggested that 6-8 wt% hydrogen storage in HCl doped polyaniline and polypyrrole at room temperature is possible. The authors attributed this unusual phenomenon to the
combined effects of molecular sieving and metallic properties of the conducting polymer. Panella et al. [100] could not reproduce this result, and Huang et al. [101] observed a much lower hydrogen storage capacity of 1.44 wt%.

Figure 2.8: Possible mechanism for hydrogen interaction with doped polyaniline where $A^-$ represents the counteranion [98].

2.5 Summary

From the outset of this research program, it was the author's intention to develop highly sensitive gas sensors based on nanostructured materials. In this chapter, the author initially presented gas sensing mechanisms of MOS and polyaniline thin film based gas sensors while at the same time highlighting the difference between the nanostructured and bulk forms of materials for gas sensing. Then, a critical literature review was conducted for nanostructured metal oxides and polyaniline based sensors to justify the author's rationale for proposing them for gas sensing. The author believes that for nanostructured materials, structural morphology, orientation, crystallinity, film porosity and operating temperatures must be optimised in order to obtain the best possible gas sensing performance. Therefore, to achieve this, the films must be investigated using various characterisation techniques such as SEM, TEM, XRD etc. and undergo electrical testing to determine the optimal operating temperatures for maximum sensitivity.
REFERENCES


Chapter 3

Theoretical Background of SAW Sensors

3.1 Introduction

In Chapter 2, from a critical review of literature it was revealed that nanostructured materials have the potential to improve performances of traditional gas sensors. Thus, the knowledge gained from the previous chapters has formed the basis of the author’s novel approach to develop nanostructured material based SAW and conductometric gas sensors. The purpose of this chapter is to illustrate the author’s rationale for proposing novel layered nanostructured materials/ZnO/ surface acoustic wave (SAW) substrate structures to develop highly sensitive gas sensors.

In this PhD work, the author employed both SAW and conductometric transducing platforms to develop nanomaterial based gas sensors. As the theory and design aspects of SAW sensors are much more complex than that of conductometric sensors, this chapter will only focus on SAW technology.
In order to present author’s novel nanostructured material based SAW structures, it is necessary to first demonstrate a general understanding of acoustic wave transducers and the theoretical background of acoustic wave propagation and generation in piezoelectric media, and conductometric and mass sensitivity in SAW sensors. This will chapter will cover all of these aspects. Section 3.2 is devoted to the general overview of acoustic wave devices, piezoelectric substrate materials, and SAW devices with different acoustic modes. Section 3.3 covers the derivation of the electromechanical coupling co-efficient tensor from the constitutive and governing equations for piezoelectric materials. Section 3.4 describes the operational principles of the SAW gas sensors, in particular mass and conductometric sensitivity. Section 3.5 presents the novel nanostructured material based layered SAW structures developed by the author. Finally, section 3.6 provides a summary of this chapter.

3.2 Fundamentals of Surface Acoustic Wave Sensors

3.2.1 Overview of Acoustic Wave Devices

Acoustic wave devices are so named as their transduction mechanism is based on the propagation of mechanical or acoustic waves. When the acoustic wave propagates through or on the surface of the material, any changes to the characteristics of the propagation path perturb the velocity and/or amplitude of the wave. Changes in velocity can be monitored by measuring the frequency or phase characteristics of the devices and can then be correlated to the corresponding physical or chemical quantity being measured [1].

Generally, acoustic wave devices and sensors use a piezoelectric material to generate the acoustic waves. The “piezoelectricity” refers to the production of electrical charges by the imposition of mechanical stress on a crystal and vice versa. Applying an appropriate electrical field to a piezoelectric material creates a mechanical stress. Piezoelectricity was discovered by Pierre Curie and Paul-Jacques Curie in 1880 and received its name in 1881 from Wilhelm Hankel. This exciting phenomenon remained a curiosity until 1921, when Walter Cady invented the quartz crystal resonator for stabilizing electronic oscillators [2]. Piezoelectric acoustic wave sensors apply an oscillating electric field to create mechanical waves, which propagate through the substrate and are then converted back to an electric field for measurement [1].

3.2.2 Piezoelectric Substrate Materials

The most common piezoelectric substrate materials that can be used for acoustic wave sensors and devices are quartz (SiO$_2$), lithium tantalate (LiTaO$_3$) and lithium niobate (LiNbO$_3$),
gallium arsenide (GaAs), silicon carbide (SiC), langasite (LGS), zinc oxide (ZnO), aluminum nitride (AlN), lead zirconium titanate (PZT), and polyvinylidene fluoride (PVDF) [1]. Each of the piezoelectric materials has specific advantages and disadvantages, which include cost, temperature dependence, attenuation, and propagation velocity. Even in same material, properties can be varied depending on the material cuts and orientations [3]. Comparison of piezoelectric materials is given in Table 3.1.

Table 3.1: Comparison of different piezoelectric substrate materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>Low acoustic loss</td>
<td>Low E-M coupling</td>
</tr>
<tr>
<td></td>
<td>Easy temp. compensation</td>
<td>Phase transformation</td>
</tr>
<tr>
<td></td>
<td>Max operating temp. (573°C)</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>High electro-mechanical coupling</td>
<td>High dielectric loss</td>
</tr>
<tr>
<td>LiTaO₃</td>
<td>High electro-mechanical coupling</td>
<td>High temperature coefficient</td>
</tr>
<tr>
<td>LiNbO₃</td>
<td>High electro-mechanical coupling</td>
<td>High temperature coefficient</td>
</tr>
<tr>
<td></td>
<td>Max operating temp. (300°C)</td>
<td>Lithium loss</td>
</tr>
<tr>
<td>GaPO₄</td>
<td>Max operating temp. (970°C)</td>
<td>Phase transformation</td>
</tr>
<tr>
<td>La₂Ga₅SiO₁₄ (Langasite)</td>
<td>Max operating temp. (1470°C)</td>
<td>Melting point</td>
</tr>
<tr>
<td></td>
<td>Easy temperature compensation</td>
<td></td>
</tr>
</tbody>
</table>

3.2.3 Surface Acoustic Wave Devices

Figure 3.1: A schematic diagram of a SAW device.
Piezoelectric surface acoustic wave devices were first developed by White and Voltmer in 1965 [4]. In its basic configuration, there is an input interdigital transducer (IDT) and an output IDT pattern fabricated on a planar piezoelectric substrate and separated by a gap, as shown in Figure 3.1. Application of a varying voltage to the input IDT generates acoustic waves that travel through the region called the delay line and reach the output IDT, where the mechanical displacements due to the acoustic waves create a voltage difference between the output IDT fingers [1].

SAW devices are described by the mode of wave propagation through or on a piezoelectric substrate. Surface acoustic waves are distinguished primarily by their velocities and displacement directions; many combinations are possible, depending on the material and boundary conditions, which are given below:

**Rayleigh Mode:** In 1887, Lord Rayleigh discovered the surface acoustic wave mode of propagation [5] and in his classic paper predicted the properties of these waves. Named after its discoverer, a Rayleigh wave has a longitudinal and a vertical shear component that can couple with a medium in contact with the device’s surface as shown in Figure 3.2. Such coupling strongly affects the amplitude and velocity of the wave. SAW sensors based on the Rayleigh mode have the highest gas sensitivity of the acoustic sensors reviewed [6].

**Shear Mode:** In addition to the well-known Rayleigh mode, there are a number of other acoustic modes which are able to propagate at or near the surface of solids. Those modes have certain advantages over Rayleigh modes, such as higher velocity or stronger piezoelectric coupling. For liquid media sensing applications, they are of great interest because they are able to propagate in contact with a liquid medium without radiating appreciable energy.

Transverse, or shear, waves have particle displacements that are normal to the direction of wave propagation and which can be polarized so that the particle displacements are either parallel to or normal to the sensing surface. Shear horizontal wave motion signifies transverse displacements polarized parallel to the sensing surface as shown in Figure 3.3; shear vertical motion indicates transverse displacements normal to the surface.

In the literature different modes were denoted to describe shear horizontal waves, which are given below:

- **Surface-Skimming Bulk Wave (SSBW)** – A bulk mode propagating at shallow angle to the surface.
- Leaky Surface Acoustic Wave (LSAW) or Pseudo Surface Acoustic Wave (PSAW) – A surface mode imperfectly confined by the surface, which “leaks” energy into the substrate as it propagates.

- Love Wave – An SSBW mode which is confined to the surface by a guiding layer of lower acoustic shear velocity than the substrate.

Figure 3.2: Rayleigh type surface acoustic wave [7].

Figure 3.3: Shear horizontal type surface acoustic wave [7].
3.3 Theoretical Analysis of Acoustics Waves

In a solid, an acoustic wave is generated as a result of a deformation of the material. This is caused when atoms within the material move from their equilibrium positions. After the deformation, internal restoring forces then return the material back to equilibrium [8]. In piezoelectric materials, these mechanical disturbances can be caused by an electric field, where a coupling between electrical and mechanical parameters occurs. In the following subsection the author will first introduce the stress-strain relationship in a non-piezoelectric elastic solid and then modify the relationship to consider piezoelectric effects. Although the details of theoretical interpretations of acoustic wave propagation and piezoelectric effect can be found in numerous texts [8-13], a simple and systematic derivation of the equations is included here for clarity.

Stress and Strain in Non-piezoelectric Elastic Solid

The deformation or strain of a material occurs when particles of a medium are displaced relative to each other [11]. If a displacement component of a point in a solid elastic medium is $u_i$ for the corresponding particle position vector component $x_i$ in Cartesian co-ordinate, then, stress component $T_{ij}$ (stress tensor) and strain component $S_{ij}$ (strain tensor) for this displacement can be written by the following equations [11]:

$$\frac{\delta T_{ij}}{\delta x_j} = \rho \frac{\delta^2 u_i}{\delta x_j^2} \quad i, j = 1, 2, 3$$

(3.1)

where, $\rho$ is the mass density, and $u_i$ are the components of particle displacements along $i$ direction, and

$$S_{ij} = \frac{1}{2} \left[ \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right] \quad i, j = x, y, z$$

(3.2)

It should be noted that stress tensor component $T_{ij}$ and strain tensor component $S_{ij}$ are the second order (rank) tensors.

For small deformations in a non piezoelectric elastic material there is a direct relationship between the mechanical stress and strain described by Hooke’s Law:
\[ T_{ij} = c_{ijkl} \cdot S_{kl} \quad (3.3) \]

where, \( c_{ijkl} \) is the elastic stiffness constant (fourth rank tensor), also known as Young’s modulus with unit, N/m². The tensor equation (3.3) can be reduced to a matrix equation form given below [9]:

\[
[T] = [c][S] \quad (3.4)
\]

Considering the symmetry of the tensors, the number of independent elastic constants can be reduced to 36 from 81 (3⁴) and this can be expressed in a 6x6 \([c]\) matrix, with 36 possible independent values relating the six simplified components of stress to the six simplified components of strain. Considering the crystal symmetry of a material, these 36 constants can be further reduced to 21, which is the maximum number of independent elastic constants for any crystal. A further reduction in number of constants is possible by choosing appropriate reference co-ordinate axes in relation to crystal axes. For example, in hexagonal symmetric materials such as ZnO, the number of independent elastic constants can be reduced to five, when the z-reference co-ordinate is chosen along the Z-axis of a hexagonal crystal. Lithium niobate, lithium tantalate and quartz piezoelectric come under the trigonal crystal classification with six independent elastic constants [9].

![Figure 3.4](image.png)

Figure 3.4: Relations among mechanical and electrical variables for a piezoelectric crystal. The numbers in square brackets and parentheses show the ranks of the tensors.

**Piezoelectric Interactions**

The stress-strain relations considered in the previous sub-section are not sufficient for piezoelectric materials, where the coupling between electrical and mechanical parameters has
to be included. Relations between mechanical and electrical variables for a crystal are shown in Figure 3.4. The mechanical stress, $T_{ij}$ and the electric displacement density, $D_n$ for piezoelectric materials can be written as:

$$T_{ij} = c_{ijkl}' S_{kl} - e_{mij} E_m$$ \hspace{1cm} (3.5)$$

$$D_n = e_{nkl} S_{kl} + \varepsilon'_{nm} E_m$$ \hspace{1cm} (3.6)$$

Equations (3.5) and (3.6) are known as the piezoelectric constitutive equations, where, $E_m$ is the $m^{th}$ component of the electric field $E$, $e_{mij}$ or $e_{nkl}$ is the piezoelectric constant component, $c_{ijkl}'$ is the elastic stiffness constant measured under a constant or zero electric field, $\varepsilon'_{nm}$ is the dielectric constant component measured under constant or zero strain. The values of piezoelectric constants $e_{nkl}$ or $e_{mij}$ depend on the crystal symmetry of the piezoelectric material and can have maximum 27 ($3^3$) independent constants. The number of independent piezoelectric constants can be reduced from 27 to 18 and is expressed as a ($3 \times 6$) matrix, where the elements depend on the symmetry of the piezoelectric crystal. For example, piezoelectric crystals of lithium niobate and lithium tantalate have trigonal crystallographic symmetry and their $[e]$ matrix has the following form [9]:

$$[e] = \begin{bmatrix}
0 & 0 & 0 & 0 & e_{15} & -e_{22} \\
-e_{22} & e_{22} & 0 & 0 & e_{15} & 0 \\
e_{31} & e_{31} & e_{33} & 0 & 0 & 0
\end{bmatrix} \hspace{1cm} (3.7)$$

If $\phi$ is the electric potential associated with the acoustic wave whose wavelength is much smaller than the electromagnetic wave, then the electric potential component $E_k$ can be written as [11]:

$$E_k = -\frac{\partial \phi}{\partial x_k} \hspace{1cm} (3.8)$$

Substituting equations (3.1) and (3.8) to piezoelectric constitutive equations (3.5) and (3.6) and assuming that the material has an absence of charge ($\nabla \cdot D = 0$), then:

$$\rho \frac{\partial^2 u_i}{\partial t^2} = c_{ijkl}' \frac{\partial^2 u_j}{\partial x_j \partial x_k} + e_{mij} \frac{\partial^2 \phi}{\partial x_j \partial x_k} \hspace{1cm} (3.9)$$
Equations (3.9) and (3.10) are known as wave equations and the solutions are assumed to be in the form of waves:

\[ u_i = A_i f(\tau) \quad \text{and} \quad \phi = BF(\tau) \quad i = x, y, z \tag{3.11} \]

where, \( A_i \) and \( B \) are the unknown variables, and \( f(\tau) \) and \( F(\tau) \) are the time varying functions. The time variable, \( \tau = t - ((n_i x_i)/v) \), has \( n_i \) components in the propagation direction and \( v \) is the acoustic phase velocity [14].

Substitution of equation (3.11) into the wave equations will result in the following forms:

\[ \rho v^2 A_i = e'_{jkl} n_j n_k A_i + e_{kl} n_j n_k B \tag{3.12} \]

\[ \gamma_i A_i - e'_{jk} n_j n_k B = 0 \tag{3.13} \]

where, \( \gamma_i = e_{kl} n_j n_k \). Elimination of \( B \) in equation (3.12) and further simplification using \( A_i = \delta_i^i A_i \) and \( \Gamma_i^i = e'_{jkl} n_j n_k \), yields:

\[ \left( \Gamma_i^i - \rho v^2 \delta_i^i \right) A_i = 0 \tag{3.14} \]

where,

\[ \Gamma_i^i = \Gamma_i^i + \frac{e_{jkl} n_j n_k \gamma_i}{e'_{jkl} n_j n_k} = \Gamma_i^i \left( 1 + K_i^2 \right) \tag{3.15} \]

given that

\[ K_i^2 = \frac{e_{jkl} n_j n_k \gamma_i}{\Gamma_i^i e'_{jkl} n_j n_k} \tag{3.16} \]

It is evident from the equations (3.14), (3.15) and (3.16) that the propagation velocity of the acoustic waves and the effective elastic constants of the materials have changed due to piezoelectric coupling. The effect of piezoelectricity causes a fractional increase in phase velocity of \( K_i^2/2 \) and increases the effective elastic constants by the factor of \( (1 + K_i^2) \). The term \( K_i^2 \) is called the electromechanical coupling constant tensor and is the measure of the efficiency of the coupling of the electrical and mechanical fields associated with an acoustic wave for a given piezoelectric material [13]. It may be described as a measure of the efficiency of converting electrical energy into acoustic energy and vice versa.
It was shown by Campbell and Jones [15] that electromechanical coupling could be estimated experimentally from the difference between phase velocity with a free surface boundary condition and that with an infinitely thin, perfectly conducting layer on the surface of the SAW device, from:

\[ K^2 \approx 2 \frac{\Delta v}{v_o} \]  

(3.17)

where, \( \Delta v \) is the change of SAW velocity when a free surface of piezoelectric is electrically shorted by a highly conducting metal film and \( v_o \) is the unperturbed SAW velocity. This estimate is most accurate in cases where the difference between free and a metallised surface velocity is small, and where the wave is strongly guided.

The solution of the equation (3.14) gives three phase velocities of the acoustic waves for any given direction of wave propagation. These three waves are called the quasi-longitudinal wave, the quasi-transverse wave and the quasi-shear wave and their polarization directions are mutually orthogonal with different frequency independent propagation velocities [13].

### 3.4 Principles of Operation for Surface Acoustic Wave Sensors

Conventional SAW gas sensors consist of a 2-port SAW delay line configuration with a thin film of gas sensitive material deposited onto the active surface of the device. Generally, the sensitive layer is deposited in between the input and output IDT electrodes. The inset of Figure 3.5 shows the schematic layout of a conventional SAW gas sensing structure. For a specific SAW configuration, the performance of the sensor depends on gas sensitive materials properties such as morphology, crystallography, orientation, and film thickness.

![Figure 3.5: Schematic of a conventional SAW gas sensor structure.](image-url)
The basic operating principle of a SAW sensor is the detection of small deviations in acoustic wave propagation characteristics, which are caused by the perturbations on the active surface of the device. Generally, any change in a physical property of the device surface or a thin film overlay on the surface affects either (or both) of the wave propagation parameters: velocity \( (v) \) and attenuation \( (\alpha) \). The measurement of variations in wave propagation parameters can be utilised in the construction of a SAW based sensor. In general, the acoustic wave propagation parameters can be affected (perturbed) by many factors, each of which possesses a potential sensor response [16]:

\[
\Delta \gamma = \frac{\partial \gamma}{\partial m} \Delta m + \frac{\partial \gamma}{\partial \sigma} \Delta \sigma + \frac{\partial \gamma}{\partial \mu} \Delta \mu + \frac{\partial \gamma}{\partial \eta} \Delta \eta + \frac{\partial \gamma}{\partial \epsilon} \Delta \epsilon + \frac{\partial \gamma}{\partial p} \Delta p + \frac{\partial \gamma}{\partial T} \Delta T ...
\]  

(3.18)

where, \( \gamma \) is the complex SAW propagation factor: \( \Delta \gamma = \frac{\Delta \alpha}{k} - j \left( \frac{\Delta v}{v_o} \right) \), in which \( k \) is the wave number; \( m, \sigma, \mu, \eta, \epsilon, p, \) and \( T \) represent mass, electrical conductivity, shear elastic modulus, viscosity, permittivity, pressure and temperature, respectively. A SAW sensor coated with a gas sensitive layer changes these physical properties when exposed to a target gas altering the surface acoustic wave velocity and attenuation. A sensor response may be due to a single parameter or a combination of these parameters. However, the main perturbation mechanisms such as mass-loading, elastic loading and acousto-electric changes are generally utilised for sensing applications [17-19].

In the case of a non-conductive isotropic sensitive overlay, which is considered acoustically thin \( (hk << 1) \) and perfectly elastic \( (G^* = 0) \), the layer shear modulus \( G \) \( (G = G' + jG^* \), with \( G' \) storage modulus and \( G^* \) loss modulus) can be written as:

\[
G = G' = \mu \frac{\lambda + \mu}{\lambda + 2\mu}
\]  

(3.19)

where, \( \lambda \) and \( \mu \) are the Lame constants of the film. In a SAW device surface, considering the three perturbation mechanisms (mass, elasticity and conductivity) and using these boundary conditions, the SAW velocity shift and normalised attenuation are defined as [20]:

\[
\frac{\Delta v}{v_o} = -c.m.f.o.\Delta \rho_{s} + c.f.o.h\Delta \left[ \frac{4\mu}{v_o^2} \left( \frac{\lambda + \mu}{\lambda + 2\mu} \right) \right] - \frac{K^2}{2} \Delta \left[ \frac{\sigma_s^2}{\sigma_s^2 + v_o^6 C_s^2} \right]
\]  

(3.20)

\[
\frac{\Delta \alpha}{k} = \frac{K^2}{2} \Delta \left[ \frac{v_o C_s \sigma_s}{\sigma_s^2 + v_o^6 C_s^2} \right]
\]  

(3.21)
where, $c_m$ and $c_e$ are the coefficients of mass sensitivity and elasticity of the substrate, $\rho_s$ is the mass surface density (mass per unit area) of the coating, $v_o$ is the unperturbed velocity of the SAW sensor, $f_o$ is the fundamental frequency of the SAW sensor, and the film thickness is $h$. $K^2$ is the electromechanical coupling coefficient which gives a measure of the piezoelectric strength of the medium, $\sigma_f$ is the sheet conductivity of the film ($\sigma_f = \sigma h$, where $\sigma$ is the film bulk conductivity and $h$ is the film thickness), $C_o$ is the capacitance per length of the SAW substrate material ($C_o = \varepsilon_s + \varepsilon_o$, where $\varepsilon_s$ and $\varepsilon_o$ are the permittivities of the substrate and free space, respectively), $k$ is the wave number ($k = \frac{2\pi}{\lambda}$, where $\lambda$ is the acoustic wavelength). An important parameter of the SAW substrate is the resonant sheet conductivity, $\sigma_{sr}$, that is given by:

$$\sigma_{sr} = v_o C_o = v_o (\varepsilon_s + \varepsilon_o),$$ (3.22)

Equation 3.22 can be used to define the acousto-electric effect of the acoustic propagation of the SAW device.

It should be noted that the three terms of equation (3.20) represent the changes in mass, elastic modulus and electrical conductivity of the sensing film, respectively to changes in the SAW velocity response. In contrast, in equation (3.21), the SAW attenuation is effected by a single term as a result of the acousto-electric coupling.

The first two terms of equation (3.20) arise from strictly mechanical interactions between the SAW and a thin film on the device surface: changes in the mass or Lame constants of the film alter the amount of energy it stores, which in turn perturbs the velocity of the wave. The third term of equation (3.20) and all of equation (3.21) arise as a result of acousto-electric coupling or conductivity perturbation and will be illustrated in detail in the next sub-section.

The most commonly employed sensing mechanisms in SAW sensors are mass loading and acousto-electric changes (conductometric) [17-19]. Although, the sensing mechanism of author’s proposed nanostructured material based layered SAW sensors is predominantly conductometric, it is believed a mass adsorption of gas species also takes place onto the sensing layer. A detailed discussion of mass and conductivity based sensing mechanisms is given in next two sub-sections.
3.4.1 Conductometric Sensitivity

In conductometric gas sensing applications, the interaction of the gas molecules with the sensitive layer perturbs the electrical boundary condition at the surface of the SAW device. As a result, the velocity and attenuation of the electro-mechanical waves are perturbed. The change of velocity due to a change in conductivity of a layer on the surface of the SAW transducer is the measure of conductometric sensitivity. Ricco and Martin [17] developed the basic theory of a SAW sensor responding to a conductivity change. They proposed that the change in velocity and attenuation due to the sensing layer conductivity modulation can be approximated from the equations (3.20) and (3.21) by the following relationships [18, 21-22]:

\[
\frac{\Delta v}{v_o} = -\frac{K^2}{2} \frac{1}{1 + \left(\frac{\sigma_s}{\sigma_{or}}\right)^2}
\]  

(3.23)

\[
\frac{\Delta \alpha}{k} = -\frac{K^2}{2} \frac{\sigma_s}{\sigma_{or}} \frac{1}{1 + \left(\frac{\sigma_s}{\sigma_{or}}\right)^2}
\]  

(3.24)

For the case of \(\frac{\sigma_s}{\sigma_{or}} < 1\), \(\frac{\Delta v}{v_o}\) may be approximated as follows:

\[
\frac{\Delta v}{v_o} = -\frac{K^2}{2} \left[1 - \frac{1}{2} \left(\frac{\sigma_s}{\sigma_{or}}\right)^2\right]
\]  

(3.25)

![Figure 3.6: Surface wave velocity and attenuation as a function of layer conductivity.](image-url)
The theoretical dependence of the relative changes of the SAW velocity and attenuation as a function of the sheet conductivity \( \sigma_s \) of the sensing film normalised to the resonant sheet conductivity \( \sigma_{sr} \) has been plotted in Figure 3.6 to demonstrate the acousto-electric effect on SAW propagation. The maximum rate of velocity change occurs at a critical sheet conductivity defined by \( \sigma_s = \sigma_{sr} = v_o C_o \), which coincides with maximum power dissipation into the layer. It is important to note that the conductivity sensitivity is a function of the sheet resistance of the thin layer \( \sigma_s \) and to achieve high sensitivity the sheet conductivity of the layer must be matched to the velocity-permittivity product of the SAW mode. Significant changes in the SAW conductometric sensitivity occur when the sensing film sheet conductivity is within one order of magnitude larger or smaller than the resonant sheet conductivity. In Figure 3.6, optimum operating region for highest conductometric sensitivity is shown by enclosed shaded oval.

The magnitude of the acousto-electric response or conductometric sensitivity is linearly proportional to the electromechanical coupling coefficient, \( K^2 \). Generally, the larger the \( K^2 \), the more the acoustic wave velocity is influenced by the conductivity changes at the surface of the device. By utilising an additional layer between the piezoelectric substrate and the gas selective layer, it is possible to tailor the parameters, \( K^2 \), \( v_o \) and \( C_o \). The change in \( v_o \) and \( C_o \) allow the designer to match the product \( v_o C_o \) i.e. \( \sigma_{sr} \) of the substrate to \( \sigma_s \) of the selective layer as shown in Figure 3.5, offering the possibility of increased conductometric sensitivity. However, when adding a dielectric layer, \( K^2 \) measured at the device surface (and hence sensitivity) will generally be reduced, since the surface is isolated from the piezoelectric substrate. By utilising a piezoelectric material such as ZnO, this effect is less prominent. For example, work conducted by Powell et al. [23] have shown that with a 1 µm SiO₂ layer and 24 µm wavelength, the electromechanical coupling of XZ LiNbO₃ is reduced to 1.06%, whereas for ZnO it is 2.96%.

SAW based gas sensors and their operating principles were first reported by Wohltjen and Dessy in 1979 [24]. After that, a variety of SAW sensors were developed to detect different gases, such as H₂ [25-26], SO₂ [27], CO [28], NO₂ [29] and many others. Comprehensive reviews on the development of SAW gas sensors can be found in reports by D’Amico et al [30] in 1989, Grate et al. [31] in 1993, Vellekoop [32] in 1998, Cheeke and Wang [33] in 1999, and more recently Drafts [1] and Anisimkin et al. [34] in 2001.

Niewenhuizen et al. [35] used a Si–SiO₂–ZnO–Si₃N₄ structure with copper phthalocyanine as the sensitive layer for NO₂ detection. This structure allows acoustic wave to be generated in a
non-piezoelectric silicon substrate, with a view to integration of all components on a single substrate. The silicon nitride acts as a passivation layer, preventing interaction with the reference delay line. Jakubik [36] introduced a bi-layered structure targeting hydrogen gas using a copper phthalocyanine and palladium film at room temperature. The bi-layered structure was used in an attempt to increase the sensitivity towards hydrogen gas, by changing the conductivity of the sensitive layer to match the optimum operating region of the SAW device.

Kalantar-zadeh et al. [37] demonstrated that for both strong and weak piezoelectric substrates, a dielectric or piezoelectric layer can also be used to increase the conductometric sensitivity of the SAW device by changing the operating point of the SAW to match the conductivity sensitivity of the layer. They reported that by depositing a TiO$_2$ sensitive layer over a layered SiO$_2$/ST-cut quartz structure, a remarkably high sensitivity towards oxygen can be achieved [38]. This structure utilised the SiO$_2$ as an intermediate dielectric layer, sandwiching the IDTs between the substrate and SiO$_2$ layer. Kalantar-zadeh et al. [39-41] also demonstrated that by utilising a ZnO layer, SAW device sensitivity is greatly improved over both non-layered and SiO$_2$ layered structures. Their work showed that replacing the SiO$_2$ dielectric layer with the ZnO piezoelectric layer had the added benefit of providing higher sensitivity towards oxygen and propane.

Kalantar-zadeh et al. [23, 37] extended their work to study the effect of conductometric changes on different modes of propagation in blank XZ LiNbO$_3$ and layered ZnO/XZ LiNbO$_3$ SAW structures using the multi-layered spectral Green’s function. They found that before ZnO thin film deposition the propagation mode in the blank XZ LiNbO$_3$ substrate is a Rayleigh type, whereas after the ZnO layer deposition, an additional shear horizontal (SH) mode (Love wave) is generated and the coupling between the IDT and the acoustic modes also increased. By calculating the effective permittivity on the active surface of the device as the reference plane, and extracting the value of $K^2$ from this curve, they demonstrated that in a layered SAW structure, the device sensitivity for the Rayleigh mode is approximately 27 times larger than SH mode. To verify the theoretical findings with the experimental gas sensing results, they deposited InO$_x$ and WO$_3$ selective layers for H$_2$ and NO$_2$ sensing and good agreement of the theoretical calculations and experimental results was achieved. They also optimised the intermediate ZnO layer thickness for the maximum device sensitivity and found that it occurs when the layer thickness is either 0.5 or 1 µm.

The thickness of the intermediate layer can be optimised to match the operating point of the SAW to the conductivity of the sensitive layer to increase the device’s conductometric sensitivity. Powell et al. [42] numerically calculated SAW sensitivity of a layered ZnO/LiTaO$_3$
transducer using the Green’s function. They fabricated devices with the ZnO guiding layer thickness ranging from 0 to 8 µm yielding operating frequencies between 101.5 and 78.5 MHz. They reported that $K^2$ have a maximum value of 7.5% at a normalised layer thickness of $h/\lambda_s = 0.05$, where $h$ is the ZnO layer thickness and $\lambda_s$ is the period of the IDT electrode pairs. Ippolito [43] reported that the addition of a conductive catalyst such as Au or Pt to a WO$_3$ sensitive layer in a ZnO/36° YX LiTaO$_3$ layered SAW structure can increase the device sensitivity by as much as 50 times.

In this PhD work both layered and non-layered SAW structures were employed to develop nanomaterial based SAW gas sensors. The layered structures were formed by depositing an intermediate ZnO layer on 64° YX LiNbO$_3$ and 36° YX LiTaO$_3$ substrates. A sensitive layer which interacts with the analyte was added on top of this intermediate or selective layer. The functionality and requirements of the intermediate and sensitive layers are separate. To achieve high conductometric SAW sensitivity, the main focus in choosing an intermediate layer is to increase the overall $K^2$ of the layered SAW substrate, whereas the choice of selecting a sensitive layer is depend on the target gas and its sensitivity towards that analyte.

Although SAW sensing technology is mature, many research groups are still working to improve the performances of SAW sensors for commercial sensing applications, such as the use of nanomaterials as sensitive layers. Recently, the author of this thesis has developed a novel polyaniline nanofiber based ZnO/64° YX LiNbO$_3$ layered SAW sensor for H$_2$ sensing [44]. At first, hydrochloric acid (HCl) and camphor sulfonic acid (CSA) doped polyaniline nanofibers with an average diameter of 30 and 50 nm, respectively, were synthesized using the rapidly mixed reaction method. Then, polyaniline nanofiber based layered ZnO/64° YX LiNbO$_3$ structures were developed and investigated for gas sensing applications and for the first time nanofiber diameters have been linked to hydrogen gas responses. The author has extended his work to develop novel polyaniline nanofibers and In$_2$O$_3$ nanoparticle nanocomposite based layered SAW sensors and found that it is highly sensitive towards H$_2$, CO and NO$_2$ gases [45]. For both sensors, the intermediate ZnO piezoelectric layer is used to shield the IDTs from a highly conductive polyaniline nanofiber and its nanocomposite sensitive layer, without sacrificing sensitivity.

By using a piezoelectric ZnO intermediate layer on substrates with high $K^2$ values (between 3 and 5.5%), such as 64° YX LiNbO$_3$ and 36° YX LiTaO$_3$, significant improvements in conductometric SAW sensitivity were achieved utilizing both Rayleigh and SH-SAW modes. Additionally, the application of nanostructured material based sensitive layers on these layered SAW structures further increase the sensor sensitivity.
3.4.2 Mass Sensitivity

Mass sensitivity is defined as the frequency shift caused by the addition of a mass (thin film of materials, chemical species etc) onto the surface of a SAW device. Mass sensitivity is related to the device structural geometry, operating frequency, properties of the substrate and the nature of the acoustic waves. It is also strongly related to the surface confinement; i.e. the guiding of acoustic energy near the surface. Applications are found in areas such as film thickness monitoring, gas and liquid media sensing and bio-sensing. From equation (3.20), mass sensitivity in terms of velocity change can be defined as:

\[
\left( \frac{\Delta v}{v_o} \right)_{mass} = -c_m f_o \Delta \rho_s
\]  

(3.26)

In practice, stiffness, viscosity and geometry of the material also affect the response, particularly if the layer thickness is a significant fraction of the acoustic wavelength. The most widely used definition of the mass sensitivity of a SAW mode is [46]:

\[
S_m^o = \lim_{\Delta m \to 0} \left( \frac{\Delta v / v_o}{\Delta m / a} \right)
\]  

(3.27)

where, \( v_o \) is the unperturbed SAW phase velocity and \( \Delta v \) is the velocity change due to mass change per unit area (\( \Delta m / a \)). In practice, it can be regarded as the fractional velocity change due to the addition of a small mass per unit area, and is commonly expressed in \( \text{cm}^2/\text{g} \). Since frequency is typically the parameter which is experimentally measured, the corresponding sensitivity in terms of the output frequency is defined as [47-48]:

\[
\left( \frac{\Delta f}{f_o} \right)_{mass} = \left( \frac{\Delta v}{v_o} \right)_{mass} = -c_m f_o \Delta \left( \frac{m}{a} \right)
\]  

(3.28)

\[
S_m' = \lim_{\Delta m \to 0} \left( \frac{\Delta f / f_o}{\Delta m / a} \right) = \left( \frac{v_g}{v_o} \right) S_m^o
\]  

(3.29)

where, \( v_g \) is the group velocity of the SAW mode, which can be calculated from the phase velocity.

SAW devices based on a mass based sensing mechanism are generally employed for liquid sensing applications. However, there are reports on gas sensors to detect volatile organic
compounds (VOC) and humidity [49-51]. In gas phase sensing applications, both the Rayleigh and Love wave mode in a SAW sensor can be utilised as they are strongly guided by the substrate surface and highly sensitive towards mass perturbations. However, the mass sensitivity of Love wave sensors can be greater than that of Rayleigh wave devices, because the use of a thin guiding layer in Love wave devices provide higher acoustic wave confinement at the device surface when compared to non-layer Rayleigh wave sensors [16, 41]. Love mode devices supports a SH-SAW polarisation, thus particle displacement is perpendicular to the surface plane of the device and can be used for both liquid and gas sensing applications.

Jacoby et al. [49] developed a Love mode SAW mass sensor using a polymer sensitive layer and found that it is highly sensitive towards organic vapour due to the gas absorption on the polymer layer. Zimmermann et al. [50] developed and successfully applied a Love mode device to detect organophosphorous vapours, and achieved approximately 10 times the sensitivity of a Rayleigh wave sensor operating at a similar frequency. Kovacs et al [47] have numerically analysed the mass sensitivity of a layered SAW device operating in the first few Love modes for an ST-quartz substrate with a sputtered SiO₂ guiding layer. It was shown that there existed an optimal thickness for the guiding layer, where gravimetric sensitivity, reached a maximum for a given wavelength.

Wang et al [52] reported that the maximum mass sensitivity of a Love mode device can be 20 times higher than that of the SH-SAW device fabricated on the same substrate and operating at the same frequency. It has been shown that replacing the SiO₂ layer with ZnO, which is a piezoelectric material, results in considerable improvement of mass sensitivity [40, 53]. Shoji et al. [53] showed that deposition of a ZnO layer on LiNbO₃ or LiTaO₃ results in an improved electromechanical coupling coefficient ($K^2$). Recently, Penza et al. [51] reported a novel layered SAW sensor based on a carbon nanotube sensitive layer in SiO₂/ST quartz substrate for organic vapour detection. In this case, the SiO₂ layer prevents short circuiting of the IDT patterns by the conductive nanotubes, and protects the IDTs from direct exposure to the analyte. This mass sensitivity can be important even in cases where it is not desired such as conductometric response, since it can lead to interference in the response.

### 3.5 Proposed Layered SAW Gas Sensor Structures

The author has developed novel nanostructured material based SAW gas sensors employing layered nanomaterials/ ZnO/ SAW substrate structures. Layered SAW devices were fabricated by depositing an intermediate ZnO thin film onto the conventional SAW substrate.
such as $64^\circ\ YX\ LiNbO_3$ and $36^\circ\ YX\ LiTaO_3$. A sensitive nanostructured material layer was then deposited on top of the intermediate ZnO layer as shown in Figure 3.7. The nanostructured material film covers the entire device surface and interacts with gas species.

The sensing mechanisms of the developed novel layered SAW devices are mainly based on the conductivity variation on the nanomaterial layers. As the thin films based on nanostructured materials are porous and have high surface to volume ratio’s (see Chapter 1 and 2), it is expected that the conductivity of the sensitive layer will be highly modulated by gas species. The sensitivity of the layered SAW devices mainly depends on the scale of conductivity variations in the sensitive layer. Thus, the author believes that by employing nanostructured materials on the sensitive layer, the performances of the conventional layered and non-layered SAW sensors can be greatly enhanced.

The intermediate layer thickness and material properties are also important parameters that affect the sensor performances and stability. The choice of ZnO as an intermediate layer and the optimum 1.2 µm ZnO thickness to fabricate layered SAW structure, were inspired from the works done by Kalantar-zadeh et al. [39-41], Powell et al. [42] and Ippolito et al. [43] as mentioned in sub-section 3.4.1. In this thesis, layered SAW structures were chosen over conventional non-layered SAW structures to develop nanomaterial based sensors. The layered structures offer a number of advantages compared to non-layered structures:

- A highly conductive sensitive layer such as conductive polymer may inhibit device oscillation due to the short circuited IDTs (metal patterns). Thus an appropriate intermediate layer can provide isolation between the sensitive layer and the IDTs to ensure reliable device oscillation.
A layer of inert material (ZnO or SiO₂) protects the IDT electrodes from a harsh gas environment, which improves both short and long term stability.

An intermediate piezoelectric layer above the IDTs increases electromechanical coupling, which allows fabrication of devices with reduced insertion loss and high sensitivity compared to non-layered structures.

In this work, the author employed doped polyaniline nanofibers as a sensitive layer which is highly conductive. Thus, in polyaniline nanofiber and polyaniline/metal oxide nanocomposite fibre based layered SAW sensors, the ZnO intermediate layer acts as a protective layer to prevent IDTs from being short circuited. In addition, ZnO seed layer is prerequisite to grow ZnO nanorods on ZnO/64° YX LiNbO₃ layered structures which will be described Chapter 5.

A shear-horizontal (SH) leaky SAW propagation is the dominant mode in 36° YX LiTaO₃ and 64° YX LiNbO₃ substrates. After the deposition of the intermediate ZnO layer, the SH leaky mode is retained. Both layered substrates have high electromechanical coupling coefficients, which result in high conductometric sensitivity compared to non-layered structures.

Previous work on layered SAW sensors employed polycrystalline semiconducting metal oxides or conventional conducting polymers as a sensitive layer. The author’s novel idea is to combine the advantages of layered SAW structures and nanostructured materials to maximise the device performance. To the best of the author’s knowledge, the proposed layered nanostructured metal oxides or conducting polymers/ ZnO/ piezoelectric substrate configurations have not previously been reported on for gas sensing applications.

3.6 Summary

From the outset of this research program, it was the author's intention to develop highly sensitive gas sensors using novel layered nanostructured materials/ ZnO/ piezoelectric substrate configurations. The knowledge gained from the critical literature review on nanostructured material based gas sensors in Chapter 2 and layered SAW structures in this chapter supports the author’s proposition for novel structures for gas sensing applications. It is believed these nanostructured material/ZnO/SAW structures will pave the way to develop the next generation of highly sensitive commercial gas sensors.

This chapter demonstrate a general understanding of acoustic wave gas sensors and the theoretical background of acoustic wave propagation and generation in piezoelectric media to
derive electromechanical coupling co-efficient. The operating principles of SAW based gas sensors were presented, highlighting the conductometric and mass based sensing mechanisms. The author’s proposed novel layered nanomaterial based SAW structures for gas sensing applications were then presented. The theoretical discussions for SAW sensors presented in this chapter were systematically compiled from the literature to gain a comprehensive understanding of the SAW sensing technology. The next chapter will discuss fabrication of SAW and conductometric transducers to develop nanomaterial based gas sensors.
REFERENCES


Chapter 3


Chapter 4

Fabrication of SAW and Conductometric Substrates

4.1 Introduction

In this chapter, the processes used to fabricate the layered SAW and conductometric sapphire transducers are described. Sections 4.2 to 4.4 will cover the fabrication of layered 64° YX LiNbO₃ and 36° YX LiTaO₃ transducers and section 4.5 will cover the fabrication of conductometric sapphire transducer structures.

There are many steps involved in the fabrication of the devices, which include: mask design, metallisation layer deposition, photolithography, thin film deposition (intermediate ZnO layer), and deposition of sensitive nanostructured metal oxide and polymer films. A fault in any of these fabrication stages could lead to an irreversible error that requires restarting the entire process.
SAW and conductometric devices were fabricated using processes that have been primarily developed for IC technology in the microelectronics industry. There are two processes commonly used: etching and lift-off. In this thesis, the author has fabricated the devices using the etching method. After fabricating the layered ZnO/64° YX LiNbO₃ and ZnO/36° YX LiTaO₃ SAW and 3x3 mm² sapphire conductometric transducers, the author has deposited or grown the sensitive nanostructure materials onto these transducers for gas sensing applications which will be detailed in next chapter.

All fabrications performed by the author were undertaken within the Microelectronics and Materials Technology Centre (MMTC) clean-room and vacuum laboratory facilities at RMIT University.

The following subsection will describe the fabrication process of the layered SAW structures, including: photolithographic masks, sample preparation, metallization, wafer dicing, photolithography, chemical etching and deposition of the intermediate ZnO layer. The fabrication process and the photolithographic mask are the same for both 64° YX LiNbO₃ and 36° YX LiTaO₃ wafer transducers.

### 4.2 SAW Transducer Fabrication Process

#### 4.2.1 Photolithographic Mask

The photolithographic mask was designed and fabricated on three and four inch rectangular quartz substrates. The IDT patterns were designed using computer-aided design (CAD) layout tools. The design files were exported as a standard GDSII stream format. The IDT patterns on the quartz plate are called positive mask.

#### 4.2.2 Sample Preparation

Thorough cleaning of the sample is a vital initial step to ensure the final success of the IDT pattern fabrication. To obtain good adhesion with uniform coating of the metallic-thin film on the wafer surface, a thorough cleaning of the bare wafer surface is necessary. Any small particle on the substrate will result in a break in the IDT finger pair or a short circuit between them.

Initially, the sample wafer was cleaned in an acetone bath for five minutes to de-grease the surface. The sample was rinsed in methanol for two minutes and deionised water for five minutes, then dried by blowing compressed nitrogen. To confirm that the wafer is highly
clean, a thorough visual inspection of the wafer surface was conducted under a microscope. If necessary, a cotton swab with methanol was used to remove any remaining contamination.

**4.2.3 Metallisation on Wafer**

Metallisation of the samples (gold/titanium) was performed using a Balzer\textsuperscript{TM} electron beam evaporator. A 20 nm thick titanium layer was first deposited onto the wafer, followed by a 80 nm layer of gold. The titanium layer was deposited first in order to obtain good adhesion to the substrate. Gold was chosen for IDT patterns as it is highly inert to most of the analytes, which greatly enhances long-term stability of the transducers.

**4.2.4 Wafer Dicing**

After Au/Ti metallisation, the sample wafers were diced to 12x12 mm\textsuperscript{2} size. A dicing saw (DAD 321) with a diamond blade was used for dicing. To protect the metallised wafer during the dicing process, a thick photoresist was first spin-coated over the wafer. After dicing, the samples were cleaned using the procedures described previously in section 4.4.2.

**4.2.5 Photolithography**

The photolithographic process was conducted in a class-1000 clean room environment with a constant temperature of approximately 22°C and a relative humidity of 40%. At first, a layer of positive photoresist (AZ1512) was spin-coated over the metallised device surface, and then soft baked at 90°C for 20 minutes. A positive photoresist becomes soluble on exposure to UV light. The spinning was performed at 3000 rpm for 30 seconds to form a photoresist layer of approximately 1.2 µm. After soft baking, the wafer was cooled to room temperature for approximately 15 minutes before the UV light exposure.

A contact mask aligner (Carl Suss MRK-3) was used to align the positive SAW mask with the photoresist coated wafer. The placement of the wafer is such that the IDT structures are parallel to the wafer reference cut (Figure 4.1). The resulting device had the acoustic propagation direction parallel to the crystallographic X-direction. After the alignment, the wafer was exposed to ultra-violet (UV) radiation for 10 seconds. The exposed wafer was subsequently developed in a mixture of AZ-400\textsuperscript{®} developer and D.I. water in a ratio of 1:4 for 15 seconds. The samples were then washed with DI water to remove any excess developer solution. Great care should be taken at this stage as under- or over developing the photoresist layer will degrade the IDT finger structures. Successful developing processes were confirmed by visual inspection of the developed wafer under an optical microscope.
After developing, a post bake was conducted at 110°C for 20 minutes to assist in the hardening of the photoresist before etching. The wafer was then allowed to cool down to room temperature for approximately 20 minutes.

Figure 4.1: Orientation of lithium niobate (64° YX LiNbO₃) with shear horizontal SAW delay line devices.

4.2.6 Chemical Etching

Figure 4.2: Summary of the photolithography process.
Wet chemical etching of the unwanted gold/titanium was performed in this stage. First, the gold layer was etched using a gold etchant of 94:6 H₂O: “Techni Strip Au” solution (17% Potassium Cyanide), followed by a thorough rinsing in DI water. The etching time is extremely critical as under-cutting of the finger pattern may occur after prolonged times, and greatly depends on etchant solution strength and may vary from sample to sample. Typically, the samples were immersed in the gold etchant for 40 to 60 seconds until a noticeable colour change occurred due to appearance of the Ti layer.

The Ti adhesion layer was then etched using a 1.5: 98.5 HF: H₂O solution for approximately 20 seconds, followed by a thorough rinsing under DI water. The photoresist layer was then stripped by immersion of the samples in heated (80°C) AZ100 for 20 minutes, followed by a rinse in deionised water. A pictorial summary of the IDT pattern fabrication process is shown in Figure 4.2.

4.3 SAW Transducer Design Parameters

![Figure 4.3: A fabricated 64° YX LiNbO₃ SAW transducer, showing two sets of identical resonators.](image)
The SAW transducer pattern was formed on 64° YX LiNbO₃ and 36° YX LiTaO₃ substrates with and without an intermediate ZnO protective layer. The substrates consisted of two-port resonators with 38 electrode pairs in the input and output IDT, 160 electrodes in each reflective grating, 700 μm aperture width and a periodicity of 40 μm. A two-port resonator structure was chosen over a delay line as its higher phase slope increases oscillation stability. The center-to-center distance between the IDTs was 1920 μm. The IDTs were formed by patterning an 80 nm layer of Au and a 20 nm Ti layer. A fabricated dual SAW transducer is shown in Figure 4.3 (bottom). A schematic representation of the SAW resonator showing IDT and reflective gratings is shown in Figure 4.3 (top).

4.4 Deposition of Intermediate ZnO Layer

The acoustic wave guiding layer material ZnO was deposited by the author using a RF magnetron sputtering system at RMIT University, Melbourne, Australia. There are many other materials that can be used as acoustic guiding layers on SAW devices such as SiO₂. However, ZnO has certain advantages compared to the other materials as discussed in Chapter 3, section 3.4 of this thesis [1-3].

4.4.1 ZnO Thin Film Deposition

In past years, many researchers have investigated thin film fabrication processes for ZnO, including sputter deposition, chemical vapour deposition, thermal evaporation, and sol-gel deposition. Among these processes, sputter deposition of ZnO thin films has received much attention for its advantages: low substrate temperatures (down to room temperature), good adhesion of films on substrates, high deposition rates, good thickness uniformity and high density, good controllability and long-term stability [7].

In this work, a RF magnetron sputterer was used to deposit ZnO layer on the SAW substrates. Sputter deposition was performed by the author using optimum parameters from standard procedures used by researchers at MMTC. The RF magnetron sputtering system employed for ZnO film deposition is shown in Figure 4.4.

All the layered SAW devices used for the experimental gas sensing work were fabricated with a 1.2 μm thick ZnO layer. The ZnO layer was deposited onto the surface of the 64° YX LiNbO₃ and 36° YX LiTaO₃ substrates from a 99.99% pure ZnO target with samples to target distance of 50 mm. The RF power was 120 W, the sputtering gas was 40% O₂ in Ar with a pressure of 10⁻² Torr, the substrate temperature was 260°C, and the deposition time was for periods of 60 minutes.
After the deposition of guiding layer, it was necessary to expose the electrical contact pads for connection to an external circuit as the ZnO layer is not conductive. The photolithography process was performed in a similar manner to that used for the electrode patterning. To etch the ZnO layer, a solution of 1:10 HNO\(_3\): H\(_2\)O was used. A silver epoxy, Epotek H-20\(^{®}\) was used to bond gold wires to the pads.

![Schematic representation of the sputtering system at MMTC, RMIT University.](image)

**Figure 4.4**: A schematic representation of the sputtering system at MMTC, RMIT University.

### 4.5 Conductometric Transducer Fabrication

Conductometric 3×3 mm\(^2\) size alumina (Al\(_2\)O\(_3\)) substrates were fabricated by collaborators in Brescia University, Italy, onto which the author of this thesis deposited nanostructured materials for gas sensing applications. The conductometric transducer consists of a Pt IDT on one side and heater on the other side. For fabrication, a 30 nm thick titanium layer was first deposited onto the wafer using an e-beam evaporator, and then a platinum layer of 150 nm was deposited. The titanium layer was deposited first in order to obtain good adhesion of Pt
onto the substrate. Platinum was chosen for IDT patterns and heater as it is highly inert to most analytes, which greatly enhances the long-term stability of the transducers. Details of conductometric transducer fabrication process are not given here as they are similar to the SAW transducer fabrication processes given in section 4.2. Figure 4.5, shows both the heater arrangement (left) and the IDT electrode structure (right) of the alumina transducer.

Figure 4.5: Mask used to fabricate the alumina based conductometric transducer, IDT electrodes (left), heater (right).

4.6 Summary

The fabrication of conductometric and layered SAW transducers has been presented in this chapter. The fabrication process comprises mask design, substrate preparation, metallisation layer deposition, photolithography, etching and wire bonding etc. For layered SAW devices, deposition parameters of the RF sputtered ZnO intermediate layer were also presented. Great care was taken to reproducibly fabricate the transducers. Additionally, adhesion of the electrodes to the substrate was successfully achieved by using Ti as an adhesion promoter and then depositing Au. Once the transducers were fabricated, Au wires bonded on the contact pads.

The author was successful in designing and fabricating layered ZnO/64° YX LiNbO₃ and ZnO/36° YX LiTaO₃ SAW transducers with minimum differences and high consistency. These transducers were then ready for deposition of nanostructured material based thin films. The synthesis of nanostructured materials and their thin film deposition onto these transducers will be described in the next chapter.
REFERENCES


Chapter 5

Nanostructured Material Synthesis

5.1 Introduction

The successful synthesis and fabrication of ZnO nanobelts and nanorods, TiO$_2$ nanoparticles, polyaniline nanofibers, and polyaniline/metal oxide nanocomposites thin films will be described in this chapter. Different synthesis processes were employed to fabricate nanostructured materials, such as ZnO nanobelts using thermal evaporation and RF sputtering, ZnO nanorods using hydrothermal methods, TiO$_2$ nanoparticles using sol-gel and polyaniline nanofibers using chemical and electrochemical polymerisations, and polyaniline/metal oxide nanocomposites using chemical polymerisation techniques. The nanostructured material films were deposited onto the surface of the SAW and conductometric transducers whose fabrication procedures were explained in Chapter 4. The developed novel nanomaterial based sensors were then investigated for their structural and electrical characterisations which will be described in Chapter 6 and 7, respectively. Additionally, for general understanding, the fundamentals of film growth and methods for achieving nanostructured materials are presented in this chapter.
Section 5.2 describes the basics for film growth, followed by an overview of different methods to achieve nanostructured materials in Section 5.3. In Section 5.4, synthesis and fabrication of ZnO nanobelts and nanorods films are given. Synthesis and fabrication of TiO$_2$ nanoparticles are given in Section 5.5. Polyaniline nanofibers and polyaniline/metal oxide nanocomposites synthesis and fabrication are described in Section 6.6.

5.2 Fundamentals for Film Growth

Growth or deposition of thin films has been a subject of intensive study for almost a century, and many methods have been developed and improved. Growth of thin films involves the processes of nucleation and subsequent growth on the substrate or growth surfaces. The nucleation process plays a very important role in determining the crystallinity and microstructure of the resultant films. For the deposition of thin films with thicknesses in the nanometer region, the initial nucleation process is even more important.

![Figure 5.1: Schematic illustration of three basic models of initial nucleation in the film growth [1].](image)
The size and the shape of the initial nuclei are assumed to be solely dependent on the change of volume of Gibbs free energy due to super-saturation, and the combined effect of surface and interface energies governed by Young’s equation [1]. In practice, the interaction between film and substrate plays a very important role in determining the initial nucleation and the film growth. Many experimental observations revealed that there are three basic nucleation modes:

1. Island or Volmer-Weber growth,
2. Layer or Frank-van der Merwe growth, and
3. Island-layer or Stranski-Krastonov growth.

Figure 5.1 illustrates these three basic modes of initial nucleation in film growth. Island growth occurs when the growth species are more strongly bonded to each other than to the substrate. Subsequent growth results in the islands coalescing to form a continuous film. The layer growth is the opposite of the island growth, where growth species are equally bound more strongly to the substrate than to each other. First, a complete monolayer is formed before the deposition of a second layer occurs. The island-layer growth is intermediate to layer growth and island growth. Such a growth mode typically involves stress developed during the formation of the nuclei or films [1].

It should be noted that the aforementioned nucleation models and mechanisms are applicable to the formation of single crystal, polycrystalline and amorphous deposits, and for inorganic, organic and hybrid materials. Whether the deposit is single crystalline, polycrystalline or amorphous, depends on the growth conditions and the substrate. Growth of single crystal films is most difficult and requires: (i) a single crystal substrate with a close lattice match, (ii) a clean substrate surface so as to avoid possible secondary nucleation, (iii) a high growth temperature to ensure sufficient mobility of the growth species and (iv) low impinging rate of growth species to allow sufficient time for surface diffusion and incorporation of growth species into the crystal structure and for structural relaxation before the arrival of next growth species.

### 5.3 Methods for Achieving Nanostructured Materials

Studies on novel physical properties and phenomena, and potential applications of nanomaterials are possible only when nanostructured materials are available with desired size, morphology, crystal structure and orientation, and chemical composition. Thus, the synthesis and processing of nanomaterials is the first and essential aspect in
nanotechnology [2-4]. The essence of one-dimensional (1D) nanostructure formation is about crystallization [5], a process that has been investigated for hundreds of years. The evolution of a solid from a vapour, liquid, or solid phase involves two fundamental steps: nucleation and growth. As the concentration of the building blocks (atoms, ions, or molecules) of a solid becomes sufficiently high, they aggregate into small clusters (or nuclei) through homogeneous nucleation. With a continuous supply of building blocks, these nuclei can serve as seeds for further growth to form large structure.

Although crystallization has been studied for hundreds of years, very little is quantitatively known about this process. It is generally accepted that the formation of a perfect nanostructured crystal requires a reversible pathway between the building blocks on the solid surface and those in a fluid phase (i.e. vapour, solution, or melt). When developing a synthetic method for growing nanostructures, the most important issue that one needs to address is the simultaneous control over dimensions, morphology (or shape), homogeneity, and uniformity [6].

There are two general approaches to the synthesis of nanomaterials and the fabrication of nanostructures: top-down and bottom-up. The bottom-up approach refers to the build-up of a nanostructure from the bottom: atom-by-atom, molecule-by-molecule, or cluster-by-cluster whereas top-down approach is opposite. The bottom-up approach has received greater emphasis in nanotechnology literature and in the past several years, a variety of chemical methods have been re-examined as the bottom-up approach for generating 1D nanostructures. Many techniques have been developed for the synthesis and formation of 1D nanostructured materials using these two approaches. For example, spontaneous growth, template-based synthesis and electro-spinning are considered as a bottom-up approach, and lithography is a top-down approach. Some of these techniques have been explored extensively (vapour solid, vapour-liquid-solid), while others have attracted far less attention. The next two sub-sections the author will describe VLS and VS processes for 1D nanostructure growth.

5.3.1 Vapor-Liquid-Solid (VLS) Growth

Understanding the growth mechanism is critical in controlling and designing nanostructures. In the early 1960s, Wagner and Ellis [7] proposed the vapor-liquid solid (VLS) process as a crystal growth mechanism for Si whiskers. A typical VLS process starts with the dissolution of gaseous reactants into nanosized liquid droplets of a catalyst metal (such as gold, iron, etc.), followed by nucleation and growth of single crystalline rods and wires. The 1D growth is
mainly induced and dictated by the liquid droplets, the sizes of which remain essentially unchanged during the entire process of belt/wire growth.

The droplet surface has a higher sticking coefficient and is therefore a preferred absorption site for incoming vapour reactants. In this sense, each liquid droplet serves as a soft template to strictly limit the lateral growth of an individual wire/belt. As a major requirement, there should exist a good solvent capable of forming liquid alloy with the target material, ideally they should be able to form eutectic compounds. All major steps involved in a VLS process are schematically illustrated in Figure 5.2.

Figure 5.2: Schematic showing the principal steps of the vapour-liquid-solid (VLS) growth technique: from initial nucleation to continued growth.

5.3.2 Vapor-Solid (VS) Growth

Vapor-phase synthesis is probably the most extensively explored approach to the formation of 1D nanostructures such as nanowires [8], nanorods [9], and nanobelts [10, 11]. Unlike the VLS method, nanostructures are formed without introducing metal catalyst. In the VS method, it is generally accepted that the control of supersaturation is a prime consideration in obtaining 1D nanostructures, because there is strong evidence that the degree of supersaturation determines the prevailing growth morphology. A low supersaturation is required for whisker growth whereas a medium supersaturation supports bulk crystal growth. At high supersaturation, powders are formed by homogeneous nucleation in the vapour phase.

In a typical process, the vapour species is first generated by evaporation, chemical reduction, and other kind of gaseous reactions. These species are subsequently transported and condensed onto the surface of a solid substrate placed in a zone with temperature lower than that of the source material. With proper control over the supersaturation factor, one could easily obtain 1D nanostructures in moderately large quantities.
In the next section, detailed synthesis processes of the nanostructured materials used to develop novel gas sensors will be given.

5.4 Synthesis of ZnO Nanostructures

Zinc oxide is an interesting II-IV compound semiconductor with a wide direct band gap of 3.4 eV at room temperature [12]. It is a widely used material in various applications such as gas sensors, UV resistive coating, piezoelectric devices, varistors, SAW devices and transparent conductive oxide electrodes [13-14]. Among the semiconductor metal oxides, ZnO was one of the earliest discovered and is the most widely applied oxide gas sensing materials due to its high mobility of conduction electrons and good chemical and thermal stability [15-16]. It is envisioned the ordered ZnO nanostructure has the potential to enhance performance of the gas sensors. As a result, interest in synthesizing well-aligned ZnO nanorods, nanobelts and nanowires on substrate keeps growing. Well aligned ZnO nanostructures have a distinct structural morphology, high surface to volume ratios and nanoscale dimensions that allow complete diffusion of carriers inside the rod which increases the intensity of redox reactions.

Low dimensional ZnO nanostructures based thin film gas sensors have been studied by a number of researchers [17-18] who reported enhanced performance compared to coarse micro-grained ZnO sensors. Numerous vapor-phase methods such as metal organic chemical vapor deposition (MOCVD) [19], pulse laser deposition [20], thermal evaporation [21], molecular beam epitaxy [22], sputtering [23] and solution methods such as cathodic electrodeposition [24], thermal decomposition [25] and hydrothermal synthesis [26] have been employed successfully for the growth of well-aligned ZnO nanorods and nanowires. Among them, the solution methods are preferred due to their low cost and low temperature synthesis and environmental friendliness [20].

5.4.1 ZnO Nanobelt: Thermal Evaporation Method

In the family of nanobelts, ZnO is probably the most extensively studied structure. In this work, zinc oxide nanobelts were synthesized by thermal evaporation of zinc oxide powders under controlled conditions without the presence of a catalyst [10]. In principle, the thermal evaporation technique is a simple process in which condensed or powder source material is vaporized at elevated temperatures, and the resultant vapor phase condenses at certain conditions (temperature, pressure, substrate, etc.) to form the desired product.
The processes was conducted in a horizontal tube furnace, as shown in Figure 5.3, which is composed of an alumina tube, a rotary pump system, and a gas supply and control system. The right-hand end of the alumina tube is connected to the rotary pump. The carrying gas (Ar) comes in from the left end of the alumina tube and is pumped out at the right end. Commercial (Alfa Aesar) ZnO powder as the source material was loaded on an alumina boat and positioned at the centre of the alumina tube, the highest temperature zone. The substrates were placed downstream for collecting growth products.

![Schematic diagram of experimental apparatus for growth of oxide nanostructures in thermal evaporation method.](image)

Several processing parameters such as temperature, pressure, carrier gas, substrate, and evaporation time were controlled and selected properly before or during the thermal evaporation. The source temperature is slightly lower than the melting point of the source material. The pressure is determined according to the evaporation rate or vapor pressure of source material. The substrate temperature usually drops with increasing distance from the position of source material. The local temperature determines the type of product to be received. It is also noted that the thermal evaporation process is very sensitive to the concentration of oxygen in the growth system. Oxygen influences not only the volatility of the source material and the stoichiometry of the vapor phase, but also the formation of product.

Thermal evaporation of ZnO powders (purity: 99.99%; melting point: 1975°C) at 1400°C and 300 Torr for 2 hours resulted in white wool-like products that formed in high yield on the surface of the alumina plate. The products were collected and dispersed in ethanol. The solution containing ZnO nanobelts was then drop cast onto the active area of the SAW devices and annealed at 100°C to form a thin film. The typical lengths of the ZnO nanobelts are in the range of several tens to several hundreds of micrometers; some of them even have
lengths on the order of millimeters. Nanostructural characterisation of these nanobelts is given in Chapter 6.

No metal catalyst particle was observed at the ends of the ZnO nanobelts, thus the VLS process may not be the dominant growth mechanism. It is assumed the ZnO nanobelt growth is likely governed by the VS process [10]. Usually, the crystalline wire-like nanostructures are not cylindrical wires but have a faceted shape that consists of certain low index crystallographic planes. It seems that surface energy minimization may play an important role in the formation of nanobelts and nanowires. These findings imply that the formation of wire-like nanostructures may be controlled by process kinetics during crystal growth. It was observed that temperature and the super-saturation ratio are two dominant processing factors in controlling the morphology of the nanobelts.

Self-catalyzed growth could be an important process in the formation of nanobelts, in which a small thin layer or even an atomically thick metal layer such as Zn is present at the growth front and acts as a catalyst, which could lead to growth [27]. The layer could be quickly oxidized after the nanobelts are exposed to air after growth.

5.4.2 ZnO Nanobelt: RF Sputtering

Zinc oxide nanobelt layers were deposited on 3×3 mm² sapphire substrates using the RF sputtering technique without the presence of a metal catalyst [28]. Initially, the sputtering chamber was evacuated to a pressure lower than 10⁻⁵ torr. Deposition of ZnO was then carried out at a pressure of 40 mtorr and an RF power of 300 W for a period of 60 minutes. The ZnO target was prepared by a conventional solid-state method from 99.9% pure ZnO powder. The sputtering process was performed under an argon (Ar) atmosphere without external heating of the substrate.

Since no metal catalyst was used in the synthesis, it is likely that the growth mechanism of nanostructured ZnO is governed by a vapour-solid process. It is believed, at first, island-shape nanoparticles of ZnO were formed on the substrate similar to Stranski-Krstanov type growth model [29]. These nanoparticles acted as nucleation sites or seeds for subsequent growth of ZnO nanobelts as the surface energy of these nucleation sites is higher than that of the flat surface.

In addition, when the sputtering power is low (for instance lower than 200 W), the deposited ZnO layer is transparent, indicating that a thin film of highly ordered crystallites has been formed. High sputtering power is needed for the formation of ZnO nanostructures which
produces a super-saturation deposition condition [28]. In this work, the ZnO films deposited at an RF power of 300 W appear white. This indicates randomly oriented nanostructures. Nanostructural characterisation of the RF sputtered ZnO nanobelt based film is given in Chapter 6.

### 5.4.3 ZnO Nanorod: Hydrothermal Method

In this work, the author grew well oriented ZnO nanorods using a hydrothermal method on layered ZnO/64° YX LiNbO₃ substrates. First, a 1.2 μm ZnO layer was deposited using RF sputtering to form layered ZnO/64° YX LiNbO₃ substrates. The sputtering parameters and deposition conditions are the same as given in Chapter 4, Section 4.4.3. This transparent ZnO layer acts as a seeding layer for the subsequent growth of the ZnO nanorods.

To grow ZnO nanorods on the layered substrate, an aqueous solution of zinc nitrate hexahydrate (Zn(NO₃)₂.6H₂O, 0.0125 M) and NaOH (0.5 M) with a mole ratio of 1:40 was prepared as the standard precursor solution. The sputtered ZnO-coated substrate was rinsed with de-ionized water, and then submerged in the precursor solution. The growth temperature was 70°C and deposition time was 60 minutes. The procedure was similar to that described in the literature [30]. After growth, the sample was rinsed with de-ionized water and dried at 60°C for several hours before characterization.

The mechanism for nanorod growth is similar for almost all solution methods where a seed layer of ZnO is usually pre-deposited on the substrate to promote nucleation and subsequent ordered nanorod growth. Supersaturation is required for crystal growth on top of seed layer [30]. It has been reported that in hydrothermal synthesis the texture of the seed surface greatly influences the morphology and alignment of the ZnO nanorod arrays. In addition, the preparation conditions such as precursor concentration, growth temperature and deposition times also influence the morphology of ZnO nanorods [26, 31].

### 5.5 Synthesis of TiO₂ Nanoparticles: Sol-gel Method

TiO₂ is one of the most interesting candidates for gas sensing and has commercially been used as a lambda sensor in exhaust pipes. In particular, titanium dioxide films have been investigated as sensors for H₂ [32–33], CO and NO₂ [34], O₂ [35], and hydrocarbons [36]. The gas sensing capability is due to changes in the film conductivity in the presence of oxidizing or reducing gases. It has been reported that addition of metal dopants to TiO₂ further improves the gas sensing performance [37], but there has been little attempt to date to optimize or understand the mechanism in these composite materials. In this work, TiO₂ and
Au nanocrystal doped TiO₂ films were deposited on the active area of 64° YX LiNbO₃ SAW devices.

The gas sensing efficiency is determined by the matrix porosity which determines the rate of gas percolation and mass transfer into the film, the conductivity of the composite which controls the redox reactions and determines the sensitivity of the transduction process, and the metal nanocrystal catalyst which can enhance adsorption and dissociation of the substrate gas. Our goal in this work is to keep the properties of the matrix metal oxide film constant while introducing a homogeneously dispersed metal catalyst.

Since ease of fabrication and scale-up are important issues for these sensors, the TiO₂ and TiO₂-Au NPs have been synthesized by conventional sol-gel processing.

**Synthesis of Colloidal Gold**

Colloidal gold was synthesized by reducing HAuCl₄ by means of tri-sodium citrate in water through the Turkevich method [38]. 1% tri-sodium citrate solution was added to a boiling water solution of 4.5x10⁻⁴ M HAuCl₄.

**Synthesis of Sol-gel Solution**

Separately, a sol-gel solution containing the TiO₂ precursor was realized. Titanium (IV) butoxide, acetylacetone and ethanol (EtOH) were mixed in 1: 1.6: 1.2 molar ratios and allowed to react under stirring for 25 minutes in a closed vial. Acetylacetone complexes the titanium (IV) butoxide molecules through a slight exothermic reaction, and reduces the rate of hydrolysis, while ethanol decreases the overall viscosity of solution.

**Synthesis of Films**

The gold suspension was first diluted in MeOH and then mixed with the mother sol-gel solution in the ratio gold suspension: MeOH: sol-gel = 1: 3: 1. In undoped films pure water was added instead of the gold sol. Further details on the synthesis of the doped films and their characterization can be found elsewhere [39].

Films were then deposited via spin coating onto the active area of 64° YX LiNbO₃ substrates at 3500 rpm for 25 seconds in a helium atmosphere. Films were also deposited on silica and silicon substrates at room temperature for XRD and ellipsometric measurements. Samples underwent thermal annealing in a tube furnace at temperatures from 100°C to 300°C, with temperature steps of 100°C for 30 minutes duration.
5.6 Synthesis of Polyaniline Nanofiber and its Composite

5.6.1 Polyaniline Nanofiber: Rapidly Mixed Method

The traditional chemical synthesis of polyaniline uses aniline, a strong acid dopant and an oxidant that is slowly added into the reaction at low temperature with thorough stirring [40]. Typically this results in an irregular granular morphology with a very small percentage of nanoscale fibers [41]. A schematic illustration of conventional polymerisation is shown in Figure 5.4.

![Figure 5.4: Traditional polymerization of polyaniline.](image)

\[
\text{Aniline} + (\text{NH}_4)_2\text{S}_8\text{O}_8 \xrightarrow{\text{H}^+\text{A}^-} \text{Polyaniline}
\]

![Figure 5.5: Polyaniline nanofiber diameter with different synthesis acids in rapidly mixed polymerization method.](image)
In recent years, many approaches have been developed to fabricate polyaniline nanofibers, namely drawing [42], template synthesis [43-44], interfacial polymerization [44-46], rapidly-mixed reactions [47], self-assembly [48-49], electrospinning [50-52], ultrasonic, ultraviolet and gamma irradiation [53-56] and electrochemical polymerization [57]. Among these approaches, a rapidly-mixed reaction is the simplest for bulk synthesis of polyaniline nanofibers without requiring any template, surfactant, special dopant, or organic solvent. Nanofibrillar morphology appears to be intrinsic during the early stages of chemical oxidative polymerization of aniline in water [41]. The secondary overgrowth of the nanofibers leads to agglomerated particles, so nanofibers can be obtained by suppressing this growth. Polyaniline nanofibers appear to form, no matter what dopant acid is used in the polymerization. However, the diameter of the nanofibers is strongly related to the dopant acid used in the polymerization process as shown in Figure 5.5 [56]. A detailed review of polyaniline nanofiber synthesis approaches can be found in references [41] and [57].

In chemical synthesis, most of the approaches for making polyaniline nanostructures often require structure-directing templates [59-61], which must be removed at the end of the reaction, resulting in very low production rate. Prof. Richard Kaner’s group in UCLA, a collaborator of this work, have first introduced a template-free, rapidly-mixed reaction approach to synthesize polyaniline nanofibers using rapid chemical oxidative polymerisation of aniline [47]. Using the rapidly-mixed polymerisation, the author has developed novel polyaniline nanofiber based layered ZnO/64° YX LiNbO₃ SAW sensors for gas sensing applications.

The polymerisation is performed in an aqueous solution where aniline is rapidly polymerised in 1M acid by the quick addition of the oxidant (ammonium peroxydisulfate ((NH₄)₆S₈O₃)) also dissolved in 1M acid. The aniline to oxidant ratio is approximately 4 to 1, and the aniline concentration is 0.5 M. Due to the immediate interaction between the monomer and the oxidant, the primary reaction product, nanofibers, is the main morphology present. After completion of the reaction, the product is collected for purification. Filtration, centrifugation or dialysis with water gives pure doped polyaniline that can be dedoped by washing or dialyzing with aqueous ammonia or sodium hydroxide. For this study, the polyaniline is cleaned in a five-step centrifugation process. Centrifugation is continued until a dense pellet forms. Resuspension is done with water on the first centrifugation, then 1M doping acid. Water is used for the remaining resuspension steps with the final pellet resuspended to 2g/L polyaniline.
The nature of the acid used in the synthetic process was found to have a significant effect on the physicochemical properties of the resulting nanofibers. The average diameter of the polyaniline nanofibers is about 30 nm when HCl is used as a dopant acid during synthesis and about 50 nm when CSA is used as the dopant acid during synthesis, with lengths up to several microns. A schematic illustration of rapidly mixed polymerisation is shown in Figure 5.6.

Doped polyaniline nanofiber dispersions were drop cast onto the active area of the transducers using a micropipette. They were then left to dry in a clean, dry environment for one day. Two types of sensors were created with a polyaniline nanofiber sensitive layer, one synthesized with HCl dopant and the other with CSA dopant. The average thickness measured for both nanofiber thin films is 0.3 µm and the deviation in thickness across the active area of SAW transducer is 0.05 µm. Nanostructural characterisation of the polyaniline nanofiber based film is given in Chapter 6.

### 5.6.2 Polyaniline Nanofiber: Electrochemical Method

Electro-polymerization of polyaniline is generally conducted in a highly acidic solution of aniline monomer as these are soluble in water under acidic conditions [62-63]. Polyaniline can be formed by the oxidation of aniline monomer at a suitable anode or working electrode. Recently, it has been reported that polyaniline nanofibers can be synthesized by an electropolymerisation method using porous supporting templates to confine the polymer [64] or with controlled nucleation and growth using a step-wise deposition [65]. The processes can be carried out in a simple three-electrode electrochemical cell, as shown in Figure 5.7. The SAW transducer was used as the working electrode and a platinum sheet served as the counter-electrode. All potential values were recorded versus the saturated Ag/AgCl reference.
electrode. The distance between the working electrode and counter-electrode was 3 cm [66]. Upon application of a constant positive potential between the working and counter electrodes, the oxidation reaction takes place and subsequently the insoluble polymerization product is deposited onto the working electrode. The electrochemical conditions, electrode materials, solvent, counterion and monomer all influence the rate of polymerisation and hence the structure of the polymer.

The author has synthesized arrays of uniform and well oriented polyaniline nanofibers by electro-polymerization with carefully chosen polymerization parameters. Polyaniline nanofibers were grown onto the SAW substrate using two step polymerisations: controlled nucleation and subsequent growth. For the controlled nucleation, in the first step of the template free polymer growth, a high current density is used to generate the necessary nucleation clusters on the substrate surface. After completion of first step, the applied potential is reduced to allow polymer to grow from the nucleation site. Then, the novel polyaniline nanofiber based 64° YX LiNbO₃ SAW sensors were investigated towards H₂ gas. Nanostructural characterisation of the film will be given in Chapter 6 and gas sensing results in Chapter 7.

![Figure 5.7: The electro-polymerisation cell.](image)

### 5.6.3 Polyaniline/semiconducting Metal Oxides Nanocomposite Fibres: Chemical Polymerization

In this work, novel polyaniline nanofibers/metal oxide nanoparticle composites have been synthesized using the chemical polymerization technique for gas sensing applications. At
first, aniline monomer was rapidly added to the 1.0 M camphorsulfonic acid (CSA) solution of metal oxide nanoparticles. The concentration of aniline monomer to metal oxides is 5 to 1 in the solution. Next, ammonium persulfate was added to the mixture and allowed to further react overnight. The product was dedoped with 1.0 M NaOH and further purified by four cycles of washing with distilled water-centrifugation. Subsequently, the nanocomposite solution was drop cast onto the active surface of the SAW transducer using a micropipette. They were then left to dry in a clean, dry environment for one day. Using the above method, the author has successfully fabricated novel polyaniline/In$_2$O$_3$ and polyaniline/WO$_3$ nanocomposite based layered ZnO/64° YX LiNbO$_3$ SAW sensors and the promising gas sensing results have been published in a well known Journal (Nanotechnology) having many citations [67]. Nanostructural characterisation of the polyaniline/metal oxide nanocomposites based film is given in Chapter 6.

5.7 Summary

In this chapter the author has presented some fundamental aspects of film growth, and mechanisms for single crystal nanostructured material growth with special emphasis on VLS and VS growth processes. Additionally, the author has explained in detail the processes to synthesize nanobelts and nanorods of ZnO, nanoparticles of TiO$_2$, nanofibers of polyaniline and nanocomposite of polyaniline/metal oxides. The author has successfully synthesized and fabricated ZnO nanorods using a hydrothermal method and polyaniline nanofibers using an electrochemical method at RMIT University. Other nanostructured materials: ZnO nanobelts, TiO$_2$ nanoparticles, polyaniline nanofibers (chemical method) and polyaniline/metal oxide nanocomposites were synthesized in collaboration with overseas researchers. However, depositions of nanostructured materials onto the surface of the SAW and conductometric transducers were performed by the author. The structural characterization results of the nanostructured material films will be presented in Chapter 6, followed by the experimental gas sensing results in Chapter 7.


REFERENCES


Chapter 6

Micro-nano Characterisation Methods & Results

6.1 Introduction

The material properties of nanostructured metal oxide and conducting polymer thin films are strongly dependant on the deposition techniques and deposition parameters, and are known to vary considerably from bulk material properties [1]. For example, synthesizing nanostructured materials with highly oriented single crystal forms require extremely precise and controlled deposition parameters. Thus, acoustic and electrical properties of the nanostructured material based thin films are directly affected by the synthesis and deposition technique and associated deposition parameters. Additionally, the properties of the nanostructured materials can be varied significantly depending on the substrate on which they are grown [2]. Thus, to understand the fundamental properties of various nanosystems, it is necessary to characterize their structures at a nanometer or atomic level. This, in turn, allows understanding of the synthesis-structure-properties relationships of nanosystems, such as nanomaterial based gas sensors.
In this PhD thesis, the author in collaboration with other institutes has successfully synthesized ZnO nanobelts and nanorods, TiO₂ nanoparticles, polyaniline nanofibers and polyaniline/metal oxide nanocomposite fibers for gas sensing applications. Based on these nanostructured materials novel SAW and conductometric devices have been developed and investigated towards different gases which will be reported in Chapter 7. Achieving the above nanostructured forms required systematic research on the deposition parameters. Every film deposited on the substrate with different deposition parameters was completely characterised. Even though hundreds of characterisation results were obtained for each synthesis and deposition process, only a selected few are described. In this chapter, the author presents characterisation results of nanostructured materials and thin films using SEM, TEM and XRD techniques.

### 6.2 Different Micro-nano characterisation Techniques

High precision characterization instruments are increasingly required to observe, measure, and tailor the properties of nanostructured materials for fundamental analysis and various potential applications [2-3]. Characterization and manipulation of individual nanostructures require not only extreme accuracy but also atomic level resolution. Tremendous efforts have therefore been given to develop and upgrade various microscopic and spectroscopic techniques that will play a central role in characterization and measurement of nanostructured materials. Some of the instruments are surface sensitive, i.e. concerned with what lies within a few Angstroms of the sample surface, while others characterize the bulk of the material. Various techniques that are most widely used in characterizing nanostructured materials include:

1. **Structural characterization**
   - (a) X-ray diffraction (XRD)
   - (b) Electron microscopy (EM)
     - I. Scanning electron microscopy (SEM)
     - II. Transmission electron microscopy (TEM)
   - (c) Scanning probe microscopy (SPM)
     - I. Scanning tunnelling microscopy (STM)
     - II. Atomic force microscopy (AFM)

2. **Chemical characterization**
   - (a) Optical spectroscopy
     - I. UV-visible spectroscopy
     - II. Photoluminescence (PL) spectroscopy
Nanomaterials and nanostructures can be analysed and characterised by any combination of the above techniques depending on the specific applications. For example, XRD has been widely used for the determination of crystallinity, crystal structures and lattice constants of nanostructured materials and thin films; SEM and TEM together with electron diffraction pattern have been commonly used for observing the images of materials and structures in nanometer scale.

In this work, the author has extensively employed SEM, TEM and XRD techniques to characterize nanostructured materials and the thin films based on these nanomaterials. The nanostructural characterization of the films has given a deep understanding of their properties, such as the morphology, crystallinity, and orientation of the nanomaterials on the film and film porosity. The characterization results are subsequently linked with the sensor electrical test results to improve performances in Chapter 7.

6.2.1 Scanning Electron Microscopy (SEM)

SEM is one of the most versatile and widely used instruments for the characterization of nanomaterials and nanostructures. It provides morphological and structural information of organic and inorganic materials at nanoscale resolution by scanning an electron probe across a specimen. The popularity of the SEM can be attributed to many factors: the versatility of its various modes of imaging, the excellent spatial resolution, the very modest requirement for sample preparation and conditioning, the relatively straightforward interpretation of the acquired images, and the high levels of automation with user friendliness.

In this PhD thesis, the author has frequently used SEM to examine the nanostructural forms of the sensing materials, film surface topography, lateral homogeneity and chemical composition. Structural characterization of the nanomaterials in terms of length, width, shape, and distribution on the film surface, as well as statistical analysis of these parameters,
were obtained. Throughout the research the author employed a high resolution SEM (Philips XL-30) fitted with an energy dispersive X-ray spectroscopy system (EDS) manufactured by Oxford Instruments. High quality nanoscale images of the sensing materials were obtained by focusing the beam condenser and objective lenses (Fig 6.1). The electron beam accelerating voltage on the instrument was varied from 10 to 30 kV. The SEM figures presented in this thesis specify the operating voltage, spot size, magnification, working distance between the sample and the electron source, the imaging mode and the scale bar. The SEM throughout the study is used in the secondary electron imaging (SEI) mode. In SEI mode, the SEM can produce very high-resolution images of a sample surface, revealing details about 1 to 5 nm in size. Additionally, SEM micrographs in SEI mode have a very large depth of field resulting in a well-defined characteristic three-dimensional appearance useful for understanding the surface structure of a sample.

Figure 6.1: Schematic diagram of an SEM set-up [4].

In SEM, the electron beam is emitted from a heated cathode filament or a field emission tip made of various types of materials, the most common is being tungsten. A voltage is applied to the filament loop causing it to heat up. The application of high voltage in the anode accelerates the electrons from the tungsten filament source towards the anode. This electron beam is focused by a condenser lens and then re-focused by an objective lens onto the specimen. The electron beam scans the specimen in a raster pattern, similar to the way an
electron gun scans the screen in a television set [4]. The beam deflection is done magnetically through magnetic fields generated by electric currents flowing through coils. As the electrons strike and penetrate the surface of the specimen, a number of interactions occur that result in the emission of secondary electrons, back scattered electrons (BSE), characteristic X-rays, and photons from the sample, and SEM images are produced by collecting the emitted electrons or photons on a cathode ray tube (CRT). A schematic representation of the SEM apparatus is shown in Figure 6.1.

The samples placed in the SEM chamber must be either conducting or coated with a thin metal layer in order to avoid electric charging by the electron beam. Additionally, scanning takes place at low pressure so that the electrons are not scattered by the gas molecules [5-6]. The introduction of a field-emission gun as a source of the electron beam in SEM, make it possible to achieve image resolution of about 0.5 nm. The detailed results of the SEM investigation of the nanomaterials are given in the later parts of this chapter.

6.2.2 Transmission Electron Microscopy (TEM)

In TEM, electrons are accelerated from an electron gun (cathode) to focus onto a thin specimen by means of the condenser lens system, and pass through the sample either undeflected or deflected. The scattered electrons are focused by an objective lens, then amplified by a projector lens, and finally produce the desired image on the screen [7]. The scattering processes experienced by electrons during their passage through the specimen provide the necessary information for imaging. A schematic diagram of a TEM set-up is shown in Figure 6.2.

TEM has the ability to provide both image and selected area diffraction pattern (SADP) from a single sample and one can switch between them by defocusing the condenser lens to produce parallel illumination at the specimen and using a selected area aperture to limit the diffracting volume [7]. To produce a SADP bright field image, the selected area diffraction (SAD) aperture shown in Figure 6.2 only allows the main un-deviated transmitted electrons to pass. In nanotechnology, SADP offers a unique capability to determine the crystal structure of individual nanomaterials, such as nanobelts and nanorods, and the crystal structures of different parts of a sample.

The most recent versions of high-resolution transmission electron microscopes (HRTEM) have the ability to characterize nanostructures with resolution as low as one angstrom (0.1 nm). Using correct operating conditions and well-prepared samples, high-resolution image characteristics are interpretable directly in terms of projections of individual atomic
positions. Thus, the HRTEM has become a powerful and crucial tool for characterising nanostructured materials.

In this PhD work, the TEM images were obtained using a JEOL 2010 and a high resolution JEOL 4000 EX TEM microscope operating at 200 kV and 400 kV, respectively for structural and interfacial analysis as well as crystal structure investigation of the nanomaterials. A detailed TEM investigation of the nanomaterials is given later.

![Schematic diagram of a transmission electron microscope (TEM)](image)

Figure 6.2: Schematic diagram of a transmission electron microscope (TEM) [4].

### 6.2.3 X-ray Diffraction (XRD)

XRD was employed to determine crystallite phases and the structural properties of the nanostructured sensing materials. In XRD, a collimated beam of X-rays, with a wavelength typically ranging from 0.7 to 2 Å, is directed onto a sample specimen, and the angles at which the beam is diffracted are measured [8]. Generally, the beam is fixed in direction and the crystal is rotated through a broad range of angles to record the X-ray pattern, which is also called diffractogram. Each diffracted X-ray signal corresponds to a coherent reflection, called Bragg reflection, from successive planes of the crystal for which Bragg’s law is satisfied.
where \( d \) is the spacing between atomic planes in the crystalline phase, \( \theta \) is the incident angle, \( \lambda \) is the X-ray wavelength, and \( n=1, 2, 3, \ldots \) is an integer that usually has the value \( n=1 \).

The diffraction angles of the X-ray beam depend on the X-ray wavelength, the crystal orientation and the structure of the crystal. The intensity of the diffracted X-rays is measured as a function of the diffraction angle \( 2\theta \) and the specimen orientation. The exact angle and intensity of a set of peaks is unique to the crystal structure being examined. Figure 6.3 shows a schematic diagram of an XRD set-up. Crystalline phases were examined by a wide angle XRD (PW1820, Philips) with a Cu-K\( \alpha \) source. The identification of nanostructured materials was achieved by comparing the X-ray diffraction patterns with the JCPDS diffraction database. A detailed XRD investigation of the nanomaterials is given later in this chapter.

![XRD set-up schematic diagram](image)

Figure 6.3: A schematic diagram of an XRD set-up.

6.3 Micro-nano Characterisation Results

In this PhD thesis, Chapter 5 presented the synthesis and deposition of the nanomaterials which were employed to develop gas sensors. In this section, nanostructural characterisation of these nanomaterials will be presented.

6.3.1 Analysis of RF Sputtered ZnO Layer

In this PhD thesis, RF sputtered ZnO thin films were deposited on SAW devices as the guiding layer or seed layer for the growth of ZnO nanorods. The sputtered ZnO film was structurally characterised using the SEM and XRD methods. The SEM image for a sputtered ZnO layer growth on bare LiNbO\(_3\) (left) and metallised gold (right) are shown in Fig. 6.4. The SEM micrograph clearly demonstrates the size and shape of the ZnO grains to be different between the metallised and non-metallised regions of the substrate. The SEM image revealed
that average diameters of ZnO particles are 40 and 90 nm on bare LiNbO$_3$ and metallised gold, respectively.

![SEM image of sputtered ZnO thin film growth on bare LiNbO$_3$ (left) and gold (right) [9].](image)

**Figure 6.4:** SEM image of sputtered ZnO thin film growth on bare LiNbO$_3$ (left) and gold (right) [9].

![XRD analysis of ZnO seed layer/intermediate layer on 64° YX LiNbO$_3$ [9].](image)

**Figure 6.5:** XRD analysis of ZnO seed layer/intermediate layer on 64° YX LiNbO$_3$ [9].

It was observed from the XRD patterns (Figure 6.5), that the ZnO thin film grows on LiNbO$_3$ substrate with c-axis alignment [10]. The strong (002) peak on the XRD pattern indicates that the c-axis orientation is normal to the substrate. The small peak which appears at 72.6° corresponds to the (004) plane.

In SAW devices, the crystalline ZnO films should have strong c-axis preferred orientation for efficient acoustic wave guiding. Usually, the crystalline quality, in particular the preferred orientation, depends on sputtering parameters and the nature of the substrate [11]. In this PhD work the author has obtained highly crystalline c-axis orientated ZnO films of 1.2 µm thickness using the set of sputtering parameters as described in Chapter 4.
6.3.2 Thermally Deposited ZnO Nanobelts Layer

Thermally grown ZnO nanobelts were characterised using SEM, TEM and XRD methods in collaboration with Georgia Tech, USA. A SEM image (Fig. 6.6) reveals that the as-grown film consists of a large quantity of wire-like nanostructures with typical lengths in the range of tens to several hundreds of micrometers; some of them even have lengths on the order of millimeters. TEM images (Fig. 6.7) reveal that the geometrical shape of the ZnO nanostructures are nanobelts. The ZnO nanobelts have a distinct structural morphology with a rectangular cross section and a uniform width along the entire length. The ripple-like contrast, observed in the TEM image, is due to elastic strain caused by the bending of the belts [12-14].

Figure 6.6: SEM image of thermally deposited ZnO nanobelts [15].

Figure 6.7: (a) TEM image of thermally deposited ZnO nanobelts, (b) High resolution TEM image with the incident electron perpendicular to the top surface of the nanobelt [1].

SEM (Fig. 6.6) and TEM (Fig. 6.7) images show that the typical thickness and width-to-thickness ratios of the ZnO nanobelts are in the range of 10 to 30 nm and ~5 to 10,
respectively. The XRD pattern (Fig. 6.8) and high resolution TEM (HRTEM) image and its associated selected area diffraction pattern (SADP) (Fig 6.7(b)) show that the ZnO nanobelts are structurally uniform and single crystalline, with two different growth directions. From XRD and HRTEM [1], it is observed that the nanobelts, growing along [0001] and enclosed by ±(2\(\overline{1}\)0) and ±(01\(\overline{1}\)0) facets, shows no defect and no dislocation (Fig. 6.7 (b)); the one growing along [01\(\overline{1}\)0] and enclosed by ±(0001) and ±(2\(\overline{1}\)\(\overline{1}\)0) facets is also dislocation free but with only a single stacking fault that is parallel to the axis and runs through out the entire length of the nanobelt [15].

![Figure 6.8: XRD pattern of thermally deposited ZnO nanobelts.](image)

From a gas sensing view point, structurally uniform and single crystalline ZnO nanobelts are preferred since the thin films made of these nanobelts have high surface to volume ratios and little chance of changing structure and phase when operated at elevated temperatures. In addition the planar distribution of the nanobelts on the surface of the substrate provides porosity on the thin film which is essential for gas sensing. The gas sensing results of the ZnO nanobelt based SAW sensor will be presented in next chapter.

### 6.3.3 RF Sputtered ZnO Nanobelts Layer

RF sputtered ZnO nanobelts were characterised using SEM and TEM methods in collaboration with Chiang Mai University, Thailand. The SEM images in Figs. 6.9 and 6.10 indicate that the as-grown ZnO layer on the substrate consists of a large quantity of wire-like nanostructures with typical lengths in the range of several micrometers. The wire-like nanostructures are not evenly distributed across the surface; instead there are islands with
thousands of nanowires. The TEM bright field image and the associated SADP of wire-like ZnO nanostructure are shown in Fig. 6.11(a) and (b), respectively. From the TEM trace analysis, it was found that the ZnO nanostructure grew along [1120] and [2110] directions on the (0001) plane [16]. The TEM image and the cross streaking of the \(\bar{1}100\) spot in the inset of Fig. 6.11(a) indicate that the geometrical shape of the ZnO nanostructures can be categorized as nanobelts. The analysis of the TEM image also suggests that the ZnO nanobelts have a distinct structural morphology characterized by a rectangular cross section and a uniform width along the length. The analysis of SEM and TEM images show that the as-grown nanobelts have a single crystal hexagonal structure with average thickness and width of about 10 nm and 50 nm, respectively.

![SEM image of ZnO nanobelts on alumina substrate in 5 μm scale](image)

Figure 6.9: SEM image of ZnO nanobelts on alumina substrate in 5 μm scale [17].

![SEM image of ZnO nanobelts on alumina substrate in 1 μm scale](image)

Figure 6.10: SEM image of ZnO nanobelts on alumina substrate in 1 μm scale [17].
In thin film gas sensors, only the surface is affected by the interactions, so sensitivity increases with decreasing film thickness and increasing surface to volume ratios. However, traditional polycrystalline thin-film metal oxide sensors operate at high temperature and their grain boundary poisoning due to retention of analyte molecules limits repeatability and long-term stability [18]. It is anticipated that the sensors based on structurally uniform one dimensional ZnO nanobelts will be promising for stable and highly sensitive gas sensors due to their high surface to volume ratios. It is also suggested that if the dimension of the nanostructured materials is less than 100 nm then they are not subject to grain boundary poisoning [19]. The gas sensing results of the RF sputtered ZnO nanobelt based conductometric sapphire sensor will be presented in next chapter.

6.3.4 Hydrothermally Grown ZnO Nanorods Layer

Figure 6.12: SEM image of ZnO nanorods on ZnO/64° YX LiNbO₃ substrate in 5 μm scale [20].
Figure 6.13: SEM image of ZnO nanorods on the interface of LiNbO$_3$ (bottom corner) and gold IDT’s (top corner) in 500 nm scale [20].

Figure 6.14: SEM image of ZnO nanorods growth on gold (Au) IDT’s in 500 nm scale [20].

Figure 6.15: SEM image of ZnO nanorods growth on LiNbO$_3$ in 500 nm scale [20].
Hydrothermally grown ZnO nanorod films were investigated using the SEM and XRD methods. The SEM images of ZnO nanorods are shown in Figs. 6.12 to 6.15 and indicate that the ZnO nanorod density and morphology are different on the metallised gold and bare LiNbO₃ surfaces. The nanorods are densely packed and vertically grown on top of gold IDTs (Fig. 6.14). On LiNbO₃, the growth direction of nanorods is not perpendicular on the surface (Fig. 6.15). The SEM image of ZnO nanorods on the interface of LiNbO₃ and gold IDT’s is shown in Figure 6.13. At the interface, the nanorods are randomly oriented.

The SEM images reveal that average diameters of ZnO nanorods are around 90 nm on gold and 40 nm on LiNbO₃, respectively. The morphologies of the nanorods conform to the morphologies of the nanoparticles on the seed layer of ZnO (Section 6.3) where the average diameters of ZnO particles are 40 and 90 nm on LiNbO₃ and gold, respectively. The ZnO nanoparticles on the SAW substrate acted as favourable sites to promote nucleation and subsequent ordered nanorod growth. The supersaturation condition on the ZnO salt solution was one of the reasons for crystal growth on top of seed layer [21]. The SEM images also reveal that the surface of the nanorod thin film is highly porous which is essential for gas sensing.

The XRD pattern of the ZnO nanorod film (Fig. 6.16) reveals that the nanorods grow on the LiNbO₃ substrate with c-axis alignment. The strong (002) peak on the XRD pattern indicates that the c-axis orientation of the nanorods is normal to the substrate. The small peak (004) which appeared on the XRD result of seed layer (Fig. 6.5) at 72.6° is not visible anymore. This indicates ZnO nanorods are only c-axis oriented and has well crystalline structures.

The SEM images confirmed that the ZnO nanorod based film is highly porous and the nanorods on the film are well oriented. Thus, it is expected that the large exposed surface
area of the nanorods to gas media and nanoscale dimensions allow a complete diffusion of carriers within the rods which in turn increases the intensity of redox reactions. The gas sensing results of the ZnO nanorod based SAW sensor will be presented in next chapter.

### 6.3.5 Sol-gel Deposited TiO$_2$ Nanoparticles Layer

The XRD patterns of deposited TiO$_2$ and TiO$_2$-Au thin films are shown in Fig. 6.17. The patterns show the micro-structural composition of TiO$_2$ and TiO$_2$-Au films annealed up to 300°C. The detectable peaks in the (a) pattern arise from (111) and (200) planes of the cubic lattice of crystalline metal gold (powder diffraction file no. 04-0784, International Centre for Diffraction Data, Newton Square, PA). The crystal size evaluated from the Scherrer equation [23] using the FWHM values of the diffraction peak was 5 nm with standard deviation of 8%. On the other hand the pattern of the un-doped TiO$_2$ film ((b) pattern) exhibited no discernible diffraction peaks.

The TEM image in Fig. 6.18 (left) shows as synthesized gold nanocrystals in water with a mean diameter 9.72 nm with 0.9 nm standard deviation (SD). The TEM image in Fig. 6.18 (right) shows the same particles homogeneously dispersed inside the TiO$_2$ matrix. The image shows there is no aggregation of Au nanoparticles inside the TiO$_2$ matrix core. The mean size of the gold particles in the matrix was obtained by counting over two hundred nanoparticles and is 9.51 ±0.89 nm, in agreement with dimensions observed for clusters in water. This indicates there is no dissolution, coalescence or morphological changes to the nanocrystals during the dispersion into the films, nor is there any effect of the annealing process on their size distribution.

![Figure 6.17: XRD spectra of TiO$_2$ and TiO$_2$-Au films annealed up to 300°C [22].](image-url)
Figure 6.18: TEM images of Au nanoparticles as synthesized in water (left) and inside the TiO$_2$ matrix (right) heated up to 300°C [22].

Figure 6.19: Optical absorbance spectra of Au nanoparticles in solution, of TiO$_2$-Au film and of TiO$_2$ film [22].

Optical absorption spectra of the TiO$_2$ film, TiO$_2$-Au film and Au nanoparticle suspension in water are reported in Fig. 6.19. The latter are characterized by the strong absorption band associated with the surface plasmon resonance (SPR) of spherical gold nanoclusters. The band is centered at 520 nm for the nanoparticle suspension in water and at 595 nm for the same nanoparticles embedded inside the TiO$_2$ matrix. The difference in SPR band positions is related to the different refractive indices of the Au nanoparticle host media: 1.34 and 2.14 of water and TiO$_2$, respectively [24]. The average refractive index of the doped, porous TiO$_2$ film was determined by ellipsometry. The film porosity was estimated using the refractive indices of the films (both measured and calculated) through the correlation proposed by Zhao [25] and Ahn [26], assuming a value of $n = 2.52$ for the refractive index of bulk TiO$_2$. 
Ellipsometric measurements performed on the samples gave thickness, refractive index and relative porosity values summarized in Table 6.1. Porosity values have been estimated by the Lorentz-Lorentz relation using 2.52 as reference refractive index for dense TiO$_2$ at 589 nm.

Table 6.1: Values of thickness, refractive index and porosity of TiO$_2$ and TiO$_2$-au films measured by ellipsometry.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Film Thickness (nm)</th>
<th>Refractive index @ 589 nm</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ @ 300°C</td>
<td>48</td>
<td>2.09</td>
<td>37</td>
</tr>
<tr>
<td>TiO$_2$-Au @ 300°C</td>
<td>48</td>
<td>2.14</td>
<td>33</td>
</tr>
</tbody>
</table>

The doping of TiO$_2$ thin films with gold nanoparticles can enhance the catalytic activity of TiO$_2$ towards analytes. In addition, nanoscale thick films with high porosity can enhance gas sensing properties of the sensors. Hydrogen sensing results of the TiO$_2$ and TiO$_2$-Au thin film based SAW sensor will be presented in next chapter.

6.3.6 Polyaniline Nanofiber Layer: Chemical Synthesis

The SEM images of the polyaniline layer deposited on the 64° YX LiNbO$_3$ (SAW) and sapphire (conductometric) substrates are shown in Figure 6.20 and 6.21, respectively. The SEM results indicate that the polyaniline layer deposited on the both SAW and conductometric transducers consists of a large quantity of wire-like nanostructures.

Figure 6.20: SEM image of chemically polymerized HCl doped polyaniline nanofibers on a SAW substrate [27].
Figure 6.21: SEM image of chemically polymerized HCl doped polyaniline nanofibers on the sapphire substrate [28].

Figure 6.22: TEM image of chemically polymerized HCl doped polyaniline nanofibers on lacey carbon grid [29].

Figure 6.23: TEM image of chemically polymerized CSA doped polyaniline nanofibers on carbon film grid [29].
The TEM images (Figs. 6.22 and 6.23) reveal that the average diameter of the polyaniline nanofibers is about 30 nm when HCl is the dopant acid during synthesis, and about 50 nm when CSA is used, with lengths up to several microns. The average thickness measured for both HCl and CSA doped nanofiber thin films is 0.3 µm and the deviation in thickness across the active area of the SAW transducer is 0.05 µm [29].

As doping and dedoping of the nanofibers did not change the morphology of the fibers, the average diameter of the both HCl doped and dedoped polyaniline nanofibers is almost the same, 50 nm. Using a profilometer, the average thickness of the nanostructured films on the substrates was measured for both HCl doped and dedoped fibers as 0.3 µm, and the deviation in thickness across the active area of the sensors is 0.05 µm [28].

6.3.7 Polyaniline Nanofiber Layer: Electro-chemical Synthesis

![SEM images](image)

Figure 6.24: SEM images of electrochemically grown polyaniline nanofibers onto a gold surface: growth sequence from (a) to (d) [30].

Electrochemically grown polyaniline nanofibers were characterised using SEM in collaboration with the Shanghai Institute of Ceramics, China. The SEM images of polyaniline nanofibers on a gold surface are given in Figure 6.24 with growth sequence from (a) to (d). The images reveal that the polymerisation started with controlled nucleation (Fig. 6.24(a))
and then growth of the fibers from these nucleation sites (Figs 6.24(b), (c), and (d)). SEM images also show that the average diameter of the electrochemically grown polyaniline nanofibers is around 20 nm and they are connected together in a network with upward protrusion at the node. It is worth mentioning that the final size distribution of the nanofibers strongly depends on the kinetics of the nucleation and growth [31].

SEM images have confirmed that polyaniline nanofibers with a cylindrical morphology form porous structures when deposited as thin films. Polyaniline nanofibers, with diameters in the nanometer range, possess larger surface areas per unit mass compared with traditional polyaniline which is highly agglomerated [32]. The three-dimensional porous structure of a polyaniline nanofiber film allows easy diffusion of gas molecules into and out of the film and the nanoscale fiber diameters lead to rapid diffusion of gas molecules into the polyaniline [33]. Thus, it is expected polyaniline nanofiber based sensors will have enhanced performance in terms of sensitivity and dynamic response upon exposure to a target analyte.

In addition, sensitivity of a polyaniline nanofiber sensor is independent of film thickness, due to the porous structure of the film which leads to the predominance of surface phenomena over the bulk material phenomena. This advantage allows the fabrication of sensors with reproducible response that have a large tolerance to thickness variation [34].

6.3.8 Polyaniline/In$_2$O$_3$ Nanocomposite Layer

Figure 6.25: Close-up SEM image of a polyaniline/In$_2$O$_3$ nanofiber matt [35].
Chapter 6

Figure 6.26: TEM image of a polyaniline/In$_2$O$_3$ nanofiber matt [35].

Figure 6.27: Powder X-ray diffraction pattern of a polyaniline/In$_2$O$_3$ nanofiber composite (top) and a bar graph for pure In$_2$O$_3$ from the JC-PDS database (bottom) [35].

Polyaniline/In$_2$O$_3$ nanocomposite fibers were characterised using SEM, TEM and XRD methods in collaboration with UCLA, USA. SEM and TEM images of the polyaniline/In$_2$O$_3$ nanocomposite are shown in Figs. 6.25 and 6.26, respectively. The SEM and TEM images revealed that the average diameter of polyaniline/In$_2$O$_3$ nanocomposite fibers is 90 nm. TEM image also revealed that the average diameter of the In$_2$O$_3$ nanoparticles is 55 nm and they are embedded into the polyaniline nanofibers matrix. The nanofibers are connected together in a network having porosities on the film. The average thickness measured for the nanocomposite thin film using a profile meter is 0.4 µm and the deviation in thickness across the active area of SAW transducer is 0.05 µm.
An XRD pattern of the nanocomposite film is shown in Fig. 6.27, in which the sharp peaks are due to $\text{In}_2\text{O}_3$ and the broader peaks at $2\theta \sim 26^\circ$ are due to polyaniline [36]. The diffraction peaks from the nanocomposite sample are well matched to the sharp lines from the pure standard $\text{In}_2\text{O}_3$ (shown below the polyaniline/$\text{In}_2\text{O}_3$ diffraction pattern) indicating that the sample contains $\text{In}_2\text{O}_3$ particles.

### 6.3.9 Polyaniline/WO$_3$ Nanocomposite Layer

Polyaniline/ WO$_3$ nanocomposite fibers were characterised using SEM, TEM and XRD methods in collaboration with UCLA, USA. The SEM and TEM images of the nanocomposite are shown in Figs. 6.28 and 6.29, respectively. The average diameters of the nanofibers are 90 nm and they are connected together in a network. From the TEM image, it was found that the average diameter of the WO$_3$ nanoparticles is 20 nm and they are embedded in the polyaniline nanofibers backbone.
From SEM image, it can be concluded that the deposited thin film is porous. The average thickness of the polyaniline/WO$_3$ nanofiber layer on the substrate was measured by a profile meter is 0.4 µm.

An XRD pattern is shown in Fig. 6.30, in which the Bragg markers (bottom) are due to the pure WO$_3$ from the JCPDS database and the experimental reflections (above) are due to the polyaniline/WO$_3$ nanocomposite samples. The diffraction peaks from the nanocomposite sample well match the sharp lines from the pure WO$_3$, which indicate the sample contains WO$_3$ particles.

### 6.3.10 Polyaniline/SnO$_2$ Nanocomposite Layer

![SEM image of polyaniline/SnO$_2$ nanofibers](image)

Figure 6.31: SEM image of polyaniline/SnO$_2$ nanofibers [38].
Figure 6.32: TEM image of polyaniline/SnO$_2$ nanofibers [38].

Figure 6.33: XRD characterization of polyaniline/SnO$_2$ nanofibers (top) and standard JCPDS of SnO$_2$ (below) [38].

Polyaniline/ SnO$_2$ nanocomposite fibers were characterised using SEM, TEM and XRD methods in collaboration with UCLA, USA. The SEM and TEM images of the nanocomposite are shown in Figs. 6.31 and 6.32, respectively. The images revealed that polyaniline/SnO$_2$ nanofibers on the substrate have average diameters of 90 nm, while the average diameter of the SnO$_2$ nanoparticles is 25 nm, and they are embedded into the polyaniline nanofibers matrix as nanoparticle clusters. The average thickness of the polyaniline/WO$_3$ nanofiber layer on the substrate measured by a profile meter is 0.4 µm.
The XRD result is shown on Fig. 6.33, in which the Bragg markers (bottom) are due to the pure \( \text{SnO}_2 \) from JCPDS database and the peaks on the above are due to the polyaniline/\( \text{SnO}_2 \) nanocomposite. The diffraction peaks from the nanocomposite sample are well matched to the sharp lines from the pure \( \text{SnO}_2 \) standard (shown below the polyaniline/\( \text{SnO}_2 \) diffraction pattern).

Conducting polymers are used as gas sensing materials due to their room temperature operation, low fabrication costs, and ease of deposition on a wide variety of substrates [39]. Polyaniline is unique among the family of conducting polymers as its conductivity can be reversibly controlled by the protonation of the imine sites and/or the oxidation of the main polymer chain [40]. However, traditional polyaniline is not as sensitive as metal oxides towards gas species. There have been several reports on improving polyaniline’s sensitivity with methods such as synthesis of nanostructured forms [32, 34], addition of metal catalysts [41-42] and combination with other polymers [43]. In this PhD work, the author has explored the idea of combining polyaniline nanofibers with metal oxide nanoparticles for potential gas sensing applications. It is expected such composite based thin film sensors may operate at room temperature having sensitivities comparable to MOS sensors. The gas sensing results of the polyaniline/metal oxide nanocomposite fibers based SAW sensors are given in next chapter.

6.4 Summary

In this chapter, the author briefly highlighted SEM, TEM and XRD techniques used for structural characterisation of the nanomaterials and thin films. Then, the characterisation results of nanostructured thin films based on \( \text{ZnO}, \text{TiO}_2 \), polyaniline, and polyaniline/metal oxide nanocomposites were presented. It was shown how important it is to control and investigate the micro-nanostructure of the sensing materials in order to understand and improve the performance of sensors. This chapter reported on those nanostructural characteristics of the materials that are essential to correlate with gas sensing results.

Out of the three techniques used in this PhD thesis, SEM characterization of the films was first performed to attain general characteristics of the nanomaterials, such as nanomaterials morphology and orientation on the film, grain or nanostructure distribution on the film, film porosity, and defects. After the films had been inspected by the SEM, the samples were then passed for XRD characterisation. In some cases, TEM was employed for further structural analysis of the nanomaterials on the film and verification of other method results. Analysis of these three characterization data has provided complete structural properties of the
nanomaterials on the films. Once the author was confident with the nanostructured materials morphology, homogeneity, orientation, film quality and film porosity, he proceeded towards electrical characterisation of the gas sensors using the 4-channel gas calibration system.

Finally, the main conclusions that can be drawn from the above-presented structural characterisation results on nanostructured materials are:

- In 1.2 µm thick ZnO intermediate layers, the average diameters of ZnO particles are 40 and 90 nm on bare LiNbO₃ and metallised gold, respectively and the ZnO layer was grown with c-axis orientation with normal to the substrate.

- The average thickness and width-to-thickness ratios of the thermally grown ZnO nanobelts are in the range of 10 to 30 nm and ~5 to 10, respectively. In addition, the ZnO nanobelts are structurally uniform and single crystalline.

- RF sputtered ZnO nanobelts have a single crystalline structure with average thickness and width of about 10 nm and 50 nm, respectively.

- Hydrothermally grown ZnO nanorod density and morphology are different on the metallised gold and bare LiNbO₃ surfaces. The nanorods are densely packed and vertically grown on top of gold IDTs. On LiNbO₃, the growth direction of nanorods makes a non-perpendicular angle with the surface. The average diameters of ZnO nanorods are around 90 nm on gold and 40 nm on LiNbO₃, respectively.

- So-gel prepared gold doped TiO₂ films contain gold nanoparticles distributed on the surface having 10 nm average diameters. The film has 37 % porosity.

- In the chemical polymerization technique, the average diameter of the polyaniline nanofibers is about 30 nm when HCl is used as a dopant acid during synthesis and about 50 nm when CSA is used, with lengths up to several microns.

- The average diameter of the electrochemically grown polyaniline nanofibers is approximately 20 nm and they are connected in a network with upward protruding nodes.

- Polyaniline/metal oxide nanocomposites contain polyaniline nanofibers and metal oxide nanoparticles. The average diameter of polyaniline nanofibers is 90 nm and the average diameter of the metal oxide nanoparticles is 55, 20 and 25 nm for In₂O₃, WO₃, and SnO₂, respectively. The nanofibers on the thin films are connected in a network.
The nanoparticles are embedded into the polyaniline nanofibers matrix. The nanoparticle cluster formation was observed for WO₃ and SnO₂ composites.

The gas sensing system, set-up and measurement techniques as well as electrical characterisation results of nanomaterial based sensors will be presented in next chapter.
REFERENCES


Chapter 7

Sensor Testing Set-up and Results

7.1 Introduction

In this chapter, the gas sensing performance of the nanostructured material based surface acoustic wave and conductometric devices will be presented. Nanostructured ZnO (nanobelts, nanorods), TiO₂ (nanoparticles), polyaniline (nanofibers) and semi-conducting metal oxide and polyaniline nanocomposites have been synthesized and deposited onto the SAW and conductometric transducers to develop novel devices for gas sensing. The developed sensors have been tested towards various concentrations of H₂, NO₂ and CO gases. Nanostructural characterization of the films in Chapter 6 has provided information about the structural morphologies of the nanostructured materials which was the first step to evaluate film suitability for gas sensing. In this chapter, the sensing performance of the devices towards various gases will provide important static and dynamic parameters such as sensitivity, optimum operating temperature, response and recovery times and baseline stability.

The electrical measurement set-up and the testing procedures for SAW and conductometric sensors towards different gases will be presented in Section 7.2. The gas sensing results of the
thermally evaporated ZnO nanobelt based 64° YX LiNbO$_3$ and 36° YX LiTaO$_3$ SAW structures will be presented in sub-section 7.3.1. Sub-section 7.3.2 will show the gas sensing results of the RF sputtered ZnO nanobelt based conductometric alumina structures. The gas sensing results of the hydrothermally grown ZnO nanorod based ZnO/64° YX LiNbO$_3$ SAW structures will be presented in sub-section 7.3.3. Sub-section 7.3.4 will present the gas sensing results of TiO$_2$ and Au-doped TiO$_2$ based SAW structures. Sub-section 7.3.5 will present the experimental gas sensing results of polyaniline nanofiber based ZnO/64° YX LiNbO$_3$ structures. Sub-section 7.3.6 will show the gas sensing result of the electrochemically grown polyaniline nanofiber based 64° YX LiNbO$_3$ SAW sensor towards different concentrations of H$_2$. The gas sensing results of the HCl doped and dedoped polyaniline nanofiber based conductometric sensors towards H$_2$ will be presented in sub-section 7.3.7. Sub-section 7.3.8 will present the gas sensing results of the polyaniline and semiconducting metal oxides (In$_2$O$_3$, WO$_3$, and SnO$_2$) nanocomposites based ZnO/64° YX LiNbO$_3$ SAW structures.

7.2 Electrical Measurement Set-up

In this PhD work, the author has extensively employed a 4-channel gas calibration system to test the developed nanomaterial based gas sensors. The system consisted of both hardware and software components to allow for full automation. The hardware system comprises a gas chamber, an environmental chamber, amplifiers, a high resolution frequency counter, a high precision multimeter, a programmable DC power supply, computer controlled gas calibration set up, and sequence control and data acquisition computer. The test chamber was placed inside the environmental chamber for thermal, mechanical and electrical shielding. The designed system has the flexibility to control and reproduce the operational conditions of the sensors. The developed system allows both SAW and conductometric sensor electrical characterization by replacing some components. By disconnecting the amplifier assembly and replacing the frequency counter with a high precision multimeter, conductometric sensors were tested.

7.2.1 SAW Based Gas Sensor Testing Set-up

In a SAW based gas sensor, the change in electrical conductivity of the sensing layer perturbs the velocity of the propagating acoustic wave due to piezoelectric effects. The center frequency of a SAW device is given by the equation, $v = fp$ [1], where $v$ is the surface wave velocity, $f$ is the center frequency, and $p$ is the interdigitated transducer period. Therefore, the variation in velocity can be monitored by measuring the changes in resonant frequency of
the SAW device. This change in frequency is proportional to the concentration of the target analyte present in the environment.

There are few techniques for measuring the response of SAW-based sensors. A common SAW response measurement technique involves measuring the transfer function of the SAW device with a two port network analyser. In this case, one of the network analyser ports acts as a RF signal source for input IDTs and the other port acts as a vector voltmeter for measuring the amplitude and phase from output IDTs as a function of input frequency. A complete electrical analysis of the SAW device is possible by this method. The author has employed a Rohde and Schwarz ZVRE network analyser to characterize S-parameters ($S_{11}$, $S_{12}$, $S_{21}$, $S_{22}$) of the nanomaterial based SAW sensors before and after deposition of the nanomaterials on the substrate. Analysis of the S-parameters allows determination of the attenuation and phase shift of the SAW sensors over a given frequency range. The data obtained from network analyser also determines the approximate oscillation frequency of the device in an oscillator configuration set-up. However, this method is relatively expensive and has limited frequency resolution. For commercial applications, a low cost portable system for frequency and phase measurement is preferred.

This PhD work employs an oscillator configuration setup to measure the response of the SAW sensors. In this technique, the SAW sensor is used as the frequency control element with a RF amplifier in a closed loop oscillator circuit, as shown in Figure 7.1. In this configuration, RF amplifier gain compensates the losses incurred by the SAW delay line, whilst maximising the signal-to-noise ratio of the oscillator circuit.

![Figure 7.1: Feedback loop oscillator configuration.](image)

The principle of operation of oscillator configuration is well-known [2-3] and in a steady state condition the oscillator circuit is required to fulfil the following conditions [4]: 
\[ \varphi_{\text{Amp}} + \varphi_{\text{SAW}} = -2n\pi, \quad (7.1) \]

\[ |G(\omega)| |L(\omega)| = 1, \quad (7.2) \]

where, \( \varphi_{\text{Amp}} \) and \( \varphi_{\text{SAW}} \) are the phase response of the RF amplifier and SAW sensor, respectively; \( \omega \) is the angular oscillator frequency; \( |G(\omega)| \) is the magnitude of amplifier gain and \( |L(\omega)| \) is the magnitude of insertion loss of the SAW delay line; \( n \) is an integer that denotes the number of the frequency mode.

If the centre-to-centre spacing between the IDTs is \( l \), the oscillator frequency is \( f \) and the phase velocity of the acoustic waves is \( v \), then:

\[ \varphi_{\text{SAW}} = -\frac{2\pi fl}{v}, \quad (7.3) \]

Using equation 6.1, the oscillation frequency can be written as;

\[ f = \frac{\left(2n\pi + \varphi_{\text{Amp}}\right)}{2\pi l} v \quad (7.4) \]

From the above equation it is evident that to fulfil the conditions of stable oscillation, the RF amplifier must be carefully designed to provide enough forward gain to overcome the losses associated with the SAW delay line. A detailed description of the amplifier design can be found elsewhere [5].

If the amplifier is working in stable conditions and meets the closed-loop phase conditions (equation 7.1 and 7.2) with a single operating frequency, then changes in acoustic wave phase velocity (\( \Delta v \)) are proportional to changes in oscillator centre frequency (\( \Delta f \)) which can be simplified as:

\[ \frac{\Delta f}{f_o} \cong \frac{\Delta v}{v_o}, \quad (7.5) \]

where, \( f_o \) and \( v_o \) are the unperturbed oscillation frequency and surface acoustic wave phase velocity, respectively. The variation of oscillation frequency of nanomaterial based SAW sensors after exposure to analyte gases was measured using a high resolution programmable Fluke PM6680B frequency counter. The counter has a 250 ps single-shot time interval resolution with a 225 MHz range. The test system logs and measures the sensor's oscillation
frequency, \( f \) at 4 second intervals. The baseline is defined as the sensor oscillation frequency in synthetic air. The nanomaterial based SAW sensor response (\( \Delta f \)) is defined as the variation in operating frequency of oscillation due to the interaction with the target gas.

![Diagram of sensor setup](image)

Figure 7.2: Experimental set up for nanomaterial based SAW gas sensors.

A constant power supply (5 V) was applied to the amplifier and a programmable DC power supply was connected to the heater. A dual channel Agilent E3649A was employed as the DC power supply. A schematic representation of the test system connections for nanomaterial based SAW gas sensors is shown in Figure 7.2.

### 7.2.2 Conductometric Sensing Measurement Set-up

The resistance change of the nanomaterial based conductometric alumina/sapphire sensors was recorded using a high precision Keithley 2001 multimeter. A schematic representation of the test system connections for nanomaterial based conductometric gas sensors is shown in Figure 7.3.

A variable DC power supply was provided to the heater fabricated on the backside of the sensor. The test system logs and measures the sensor’s resistance, \( R \), at 4 second intervals.
The baseline is defined as the sensor resistance in synthetic air. The response, denoted as \( S \), is the ratio of resistance due to exposure of target gas with respect to the baseline. This could be defined as

\[
S_{\text{reducing}} = \frac{R_{\text{air}}}{R_{\text{gas}}}.
\]  
(7.6)

This ratio holds true for n-type nanomaterial gas sensors responding to reducing gases such as \( \text{H}_2 \) and \( \text{CO} \). However, for an n-type nanomaterial sensor, response to oxidising gases such as \( \text{NO}_2 \) is defined as:

\[
S_{\text{oxidising}} = \frac{R_{\text{gas}}}{R_{\text{air}}}.
\]  
(7.7)

Figure 7.3: Experimental set up for nanomaterial based conductometric gas sensors

### 7.2.3 Gas Delivery and Gas Cell Set-up

In order to test the nanomaterial based gas sensors, a multi-channel gas calibration system was developed based on volumetric mixing of gases using four mass flow controllers (MFCs).
The gas delivery system has the ability to accurately control and vary the concentration of four different gases simultaneously. In this PhD work, the author has employed two channels or MFCs at a time, one for synthetic air and one for the target analyte. The concentration of the gas was varied by changing the synthetic air to analyte gas ratio while maintaining a constant flow rate of 200 SCCM.

Highly pure gas cylinders of low concentration analyte gas balanced in synthetic air were used for this work. The gas cylinders were connected to the computer controlled MFCs to deliver a constant flow rate of 200 SCCM to the gas cell. The gas sensing set up consists of four MFCs, a MFC controller, a gas cell, an environmental chamber, two computers, a temperature logger, a frequency counter, a multimeter and a two channel DC power supply.

---

The gas cell was built using thick machined Teflon blocks and a fused quartz lid. The total cell volume is approximately 30 mm². The small volume of the gas chamber ensures short gas equilibrium times within the chamber, and hence, the response times can be considered to be the true response of the gas sensors. Nanomaterial based SAW and conductometric sensors were mounted inside the gas cell which was then enclosed by an environmental chamber to maintain an ambient temperature at 22°C. In the case of the SAW device, a planar micro-heater was placed beneath the sensor for heating. The micro heater was fabricated on a sapphire substrate with a patterned platinum resistive element. The heater dimension is 25x25 mm², controlled by a regulated DC power supply. A schematic of the gas cell is shown in Figure 7.4. Such an arrangement is not required for conductometric sensors as the heating element is already fabricated backside of the substrate as detailed in the fabrication chapter.

Figure 7.4: A schematic of the gas cell set-up.
7.2.4 Data Acquisition System and Testing Procedure

Custom LabVIEW-based software was developed to autonomously control the experimental setup and log the sensor’s test data from the frequency counter (SAW response) and the multi-meter (conductometric response). Data was collected by the computer via a GPIB IEEE-488 standard bus connection. The sensor responses were displayed in real-time and saved for off-line processing and analysis. The developed software has enabled the author to control the data acquisition rate, frequency counter and multimeter settings, and graphical user display set-up.

High temperatures, required to obtain optimum operating conditions for nanostructured MOS based sensors, were achieved by testing over a range of temperatures in increments of approximately 30°C. A thermocouple was used to obtain a real-time reading of the sensor surface temperature with 1°C accuracy. However, nanostructured polyaniline and polyaniline/metal oxide nanocomposite based sensors operate at room temperature, so no heating was provided.

Developed nanomaterial based gas sensors were exposed to a sequence of gas pulses (different concentrations) and this pulse sequence repeated a few times at each operating temperature until stable responses were observed. Each pulse sequence contains repetition of one concentration of analyte to test sensor’s repeatability. In most cases, repeatability and sensitivity of the nanomaterial based sensors were confirmed by testing continuously over a 7 day period. Gas exposure time was fixed for each pulse of analyte gas and the cell was purged with synthetic air for fixed periods of time between each pulse to allow the surface of the sensor to recover to atmospheric conditions. A sequence control computer was employed to automate sensor operating temperature and the pulse sequence of varying analyte concentrations.

7.3 Gas Sensing Results

Using a network analyser, frequency and phase response of the nanostructured material based SAW sensors were investigated during the fabrication process. The results obtained from the network analyser are useful to monitor the success of the fabrication process, and to know the approximate oscillation frequency and the acoustic propagation modes. The author employed the approximate oscillation frequency as a guide line to operate the SAW delay line arrangement, mentioned in previous section, with a proper oscillation frequency and acoustic mode. Stability of the oscillation frequency has also been achieved before the gas sensing test. In this chapter, frequency and phase responses of the nanomaterials based SAW sensors are
followed by their corresponding gas sensing results. The frequency and phase responses were taken by a network analyser (Rohde & Schwarz ZVRE).

### 7.3.1 Thermally Evaporated ZnO Nanobelt Based SAW Sensors

**Frequency and Phase Responses**

Figures 7.5 and 7.6 show the measured $S_{21}$ transmission parameters (log magnitude and phase) of the ZnO nanobelt based $36^\circ$ YX LiTaO$_3$ and $64^\circ$ YX LiNbO$_3$ SAW sensors, respectively before and after the deposition of ZnO nanobelts. Fabricated bare $36^\circ$ YX LiTaO$_3$ and $64^\circ$ YX LiNbO$_3$ substrates show resonant centre frequency peak at approximately 103 and 113 MHz respectively, with an insertion loss of approximately −7 to −8 dB for both. Deposition of ZnO nanobelts on a $36^\circ$ YX LiTaO$_3$ substrate shifts the resonance peak to 97 MHz with an insertion loss of -10 dB. However, very little shift in the resonance peak was observed in the case of a $64^\circ$ YX LiNbO$_3$ substrate with the increase of minimum insertion loss to -12 dB. The operational frequency of the sensors was found to be approximately 97 MHz for $36^\circ$ YX LiTaO$_3$ and 112.3 MHz for $64^\circ$ YX LiNbO$_3$ structures in dry synthetic air at room temperature.

![Graph showing frequency and phase responses of ZnO nanobelts on LiTaO$_3$ and LiNbO$_3$ substrates.](image)

Figure 7.5: Frequency and phase response of the bare $36^\circ$ YX LiTaO$_3$ and ZnO nanobelts layer on $36^\circ$ YX LiTaO$_3$ in ambient conditions.
Gas Sensing Results

Using the SAW device as a positive feedback element in a closed loop circuit with an amplifier, an oscillator was formed. A Fluke high-resolution counter (PM66860B) was used to measure the oscillation frequency. The experimental set-up and testing procedures were detailed in section 7.2. Both sensors were exposed to H\textsubscript{2} gas pulse sequences at 0.06%, 0.125%, 0.25%, 0.50%, 1%, and 0.125% concentrations in synthetic air and NO\textsubscript{2} gas pulse sequences at 0.51, 1.06, 2.12, 4.25 and 8.5 ppm concentrations in synthetic air at operating temperatures between 20°C and 200°C. A thermocouple was used to obtain a real-time reading of the sensor surface temperature with 1°C accuracy.

It was found that the ZnO nanobelt based 36° YX LiTaO\textsubscript{3} sensor had a stable response towards H\textsubscript{2} and the 64° YX LiNbO\textsubscript{3} sensor had a stable response towards NO\textsubscript{2}. Due to instability, the 36° YX LiTaO\textsubscript{3} sensor response towards H\textsubscript{2} and the 64° YX LiNbO\textsubscript{3} sensor response towards NO\textsubscript{2} did not produce meaningful results. Thus, the author has presented H\textsubscript{2} test results for LiTaO\textsubscript{3} and NO\textsubscript{2} test results for LiNbO\textsubscript{3} sensors.
Figure 7.7: Response of a 36° YX LiTaO₃ SAW based sensor towards different concentrations of H₂ gas at 185° C.

Figure 7.8: Frequency shift versus H₂ concentration (%).

Figure 7.9: Response of a 64° YX LiNbO₃ SAW based sensor towards different concentrations of NO₂ gas at 160° C.
ZnO nanobelt based sensors require an elevated operating temperature to enhance redox reactions so as to achieve the maximum sensitivity [6]. The optimal operating temperature of the 36° YX LiTaO₃ sensor for H₂ sensing was found to be 185°C, where the sensor had an operational frequency of approximately 96 MHz in synthetic air. Fig. 7.7 shows the dynamic responses of the sensor to different concentrations of H₂ gas at 185°C. The sensor response, defined as the variation in operating frequency of oscillation due to the interaction with the target gas, is 3 kHz for 1% of H₂. The response magnitude variation of the sensor to different H₂ concentrations is shown in Fig. 7.8. Frequency shift increases almost linearly with the increase of H₂ concentration.

The optimal operating temperature of the 64° YX LiNbO₃ sensor for NO₂ sensing was found to be 160°C, where the sensor had an operational frequency of approximately 111 MHz in synthetic air. Fig. 7.9 shows the dynamic responses of the sensor to different concentrations of NO₂ gas at 160°C. At this temperature the sensor response was 3.5 kHz for 8.5 ppm of NO₂. The response magnitude variation of the sensor to different NO₂ gas concentrations is shown in Fig. 7.10. Frequency shift increases non-linearly with the increase of NO₂ concentration which results in saturation at high NO₂ concentrations.

Repeatability was observed by introducing 0.12% H₂ and 0.51 ppm NO₂ twice on the gas pulse sequence as shown in Figure 7.7 and 7.9, respectively. Both of the sensors showed a slight upward trend in their baseline frequency as well as poor repeatability.

In most cases, ZnO is an n-type semiconducting metal oxide and should increase its conductivity with exposure to a reducing gas such as H₂ and decrease its conductivity with exposure to an oxidising gas such as NO₂. However, the opposite response was observed in the case of H₂, where for both H₂ and NO₂ gases, conductivity of the thermally grown ZnO
nanobelt film decreases resulting in an increase the acoustic wave velocity. Consequently, the increase in acoustic wave velocity resulted in an increase of centre frequency \( f_0 \) after exposing to \( \text{H}_2 \) gas. The reason for this anomaly is still under investigation.

7.3.2 RF Sputtered ZnO Nanobelt Based Conductometric Sensors

Gas Sensing Results

The RF sputtered ZnO nanobelt based conductometric sensor was exposed to a \( \text{H}_2 \) gas pulse sequence of 0.06%, 0.12%, 0.25%, 0.50%, 1%, and 0.12% concentration in synthetic air, \( \text{NO}_2 \) gas pulse sequence of 0.51, 1.06, 2.12, 4.25, 8.5 and 1.06 ppm concentrations in synthetic air, and propene gas pulse sequence of 0.25%, 0.50%, 1% and 0.25% concentrations in synthetic air. Gas exposure time was fixed for each pulse of analyte gas and the cell was purged with synthetic air for fixed periods of time between each pulse to allow the surface of the sensor to recover to the atmospheric condition.

The dynamic properties of the RF sputtered ZnO nanobelt based conductometric sapphire sensor such as sensitivity, stability, response and recovery times were all found to be temperature dependent. Dynamic responses of the sensor to different concentrations of \( \text{H}_2 \) at 385 and 420°C and \( \text{NO}_2 \) at 300 and 325°C are shown in Fig. 7.11 and Fig. 7.12, respectively. It was observed that with the increase of temperature, baseline resistance of the sensor was decreased and the response and recovery times of the sensor were reduced. For \( \text{H}_2 \) gas, the dynamic response was not linear with respect to gas concentrations. It is believed that at high concentrations of \( \text{H}_2 \), saturation may take place due to lack of adsorbed oxygen ions to react with analyte molecules. It is well known that in an air environment, oxygen molecules adsorb onto the surface of the ZnO layer to form \( \text{O}_2^- \), \( \text{O}^- \) and \( \text{O}^{2-} \) ions by extracting electrons from the conduction band depending on the temperature [7], [8]. Takata et al [9] found that the stable oxygen ions were \( \text{O}^{2-} \) below 100°C, \( \text{O}^- \) between 100 and 300°C and \( \text{O}^2^- \) above 300°C. The oxygen adsorptions on the surface of nanobelts can be explained by the following equations:

\[
\begin{align*}
\text{O}_2 \text{(gas)} & \rightleftharpoons \text{O}_2 \text{(ads)} \quad (7.8) \\
\text{O}_2 \text{(ads)} + e^- & \rightleftharpoons \text{O}_2^- \text{(ads)} \quad (7.9) \\
\text{O}_2 \text{(ads)} + 2e^- & \rightleftharpoons 2\text{O}^- \text{(ads)} \quad (7.10) \\
\text{O}^- \text{(ads)} + e^- & \rightleftharpoons \text{O}^{2-} \text{(ads)} \quad (7.11)
\end{align*}
\]

The positively charged ZnO surface and negatively charged adsorbed oxygen ions form a depletion region at the surface. Since ZnO nanobelts have single crystalline structure with
average thickness less than 50 nm (less than the Debye length), adsorbed oxygen can easily penetrate through the bulk of the belt. As a result, free carriers can travel through the bulk of the belt in a similar way to the channel of a field-effect transistor (FET) [10]. When the device is exposed to a target gas, two different extremes may occur: pinch-off and fully conductive states. A complete depletion of carriers inside the belt will produce a pinched-off channel. A complete removal of adsorbed oxygen from the belt produces a highly conductive channel. When an n-type ZnO nanobelt surface is exposed to a reducing gas such as hydrogen or propene at elevated temperatures, analyte molecules dissociate and combine with the adsorbed oxygen, thereby re-injecting electrons. Above 300°C, the reactions can be expressed by the following equations:

\[
H_2 \text{(ads)} + O^{2-} \text{(ads)} \underset{\text{ads}}{\overset{\text{ads}}{\longrightarrow}} H_2O + 2e^- \quad (7.12)
\]

\[
C_3H_6 \text{(ads)} + 9O^{2-} \text{(ads)} \underset{\text{ads}}{\overset{\text{ads}}{\longrightarrow}} 3CO_2 + 3H_2O + 18e^- \quad (7.13)
\]

Due to increasing concentration of electrons, the depletion region decreases to produce a conductive channel along the belt, which strongly increases belt conductivity.

In the case of NO\(_2\), a strong oxidizing gas, reactions take place directly with the oxide surface rather than with the oxygen chemisorbed at surface. During the interaction process, NO\(_2\) molecules consume conduction electrons and subsequently increase the depletion region at the surface. Thus, the ZnO nanobelt layer conductivity is reduced after exposure to NO\(_2\). The sensor response to NO\(_2\) can be explained by the following reactions:

\[
NO_2 \text{(gas)} \overset{\text{gas}}{\underset{\text{gas}}{\longrightarrow}} NO_2 \text{(ads)} \quad (7.14)
\]

\[
NO_2 \text{(ads)} + e^- \overset{\text{ads}}{\underset{\text{ads}}{\longrightarrow}} NO_2^- \text{(ads)} \quad (7.15)
\]

In this case, the sensitivity of a conductometric semiconducting oxide gas sensor is defined as:

(a) For reducing gas: \( S = \frac{[R_{\text{air}} - R_{\text{gas}}]}{R_{\text{gas}}} \) \quad (7.16)

(b) For oxidizing gas: \( S = \frac{[R_{\text{gas}} - R_{\text{air}}]}{R_{\text{air}}} \) \quad (7.17)

where, \( R_{\text{air}} \) is the resistance of the sensor in air, \( R_{\text{gas}} \) is the resistance of the sensor in presence of gas.
Figure 7.11: Dynamic response of the conductometric sensor to different H₂ gas concentrations in synthetic air at 350 and 420°C [11].

Figure 7.12: Dynamic response of the conductometric sensor to different NO₂ gas concentrations in synthetic air at 300 and 325°C [11].

Figure 7.13: Sensitivity vs operating temperature for 1% H₂ and 8.5 ppm NO₂ gas concentrations in synthetic air [11].
Figure 7.14: Sensitivity vs operating temperature for 1% propene concentration in synthetic air [11].

Figure 7.15: Dynamic response of the conductometric sensor to different H₂ gas concentrations in synthetic air at 385°C [11].

Figure 7.16: Dynamic response of the conductometric sensor to different NO₂ gas concentrations in synthetic air at 350°C [11].
The sensitivity of the sensor towards H₂ and NO₂ as a function of operating temperature is shown in Fig. 7.13 and towards propene in Fig. 7.14. The sensitivity versus operating temperature curve shows a maximum which depends on the target gas. This could be explained by the temperature dependence of the adsorption and de-sorption process on the metal oxide surface [12]. It was observed that the sensitivity towards NO₂ is highest at 220-250°C but other performance parameters such as response and recovery times are long, repeatability is poor and the base-line resistance is not stable. Therefore a trade-off between different parameters is needed in choosing the operating temperature. Analysis of the experimental results suggest that the optimum operating temperatures for the sensor are in the range of 300-400°C for H₂, 300-350°C for NO₂ and 350-420°C for propene sensing. However, it was found that the sensor has fastest response and recovery, with greater repeatability and baseline stability, at operational temperatures of 385, 350 and 370°C for H₂, NO₂ and propene gas, respectively.

Fig. 7.15, 7.16 and 7.17 show the dynamic responses of the sensor to different concentrations of H₂ at 385°C, NO₂ at 350°C and propene at 370°C, respectively. At these temperatures, the sensitivity of the sensor was calculated to be 14.3 for 1% H₂, 0.81 for 8.5 ppm NO₂ and 0.17 for 1% propene. Response (48, 180, 72 sec) and recovery (336, 268, 252 sec) times were observed for 1% H₂, 1.06 ppm NO₂ and 1% propene gas, respectively.

Reproducibility was observed as indicated when a second pulse of 0.12% H₂, 1.06 ppm NO₂ and 0.25% propene were introduced into the sensor chamber. It was found that RF sputtered ZnO nanobelt based conductometric sensor produced repeatable responses of the same magnitude with good baseline stability.
The chemisorption of gas ions onto the ZnO nanobelts is the basic gas sensing mechanism. Although, the interaction of a gas with a sensing material is primarily a surface phenomenon, the gas sensing responses of the ZnO nanobelts can not be explained on the basis of surface interaction alone. The nanobelts forms of ZnO have symmetrical tetragonal faces with greatly reduced dimensions (for thermally grown nanobelts: average thickness 20 nm and width 70 nm, for RF sputtered nanobelts: average thickness 10 nm and width 50 nm) which are comparable to the depletion layer depth. The space charge layers are thus strongly modulated by the dimensional features. Accordingly, oxygen adsorption to the nanobelt’s surface will lead to a complete depletion of conduction-band electrons with a large variation in resistance. The structural characterisation of the ZnO nanobelts in Chapter 6 and the gas sensing results of these nanorod based sensors in this chapter suggest that the developed sensors have the potential for highly sensitive commercial gas sensing applications.

### 7.3.3 Hydrothermally Grown ZnO Nanorod Based SAW Sensors

**Frequency and phase response**

![Graph](image)

Figure 7.18: Frequency and phase response of the bare 64° YX LiNbO₃, ZnO seed layer on 64° YX LiNbO₃ and ZnO nanorods on ZnO/64° YX LiNbO₃ in ambient conditions.

Figure 7.18 shows the measured S₂₁ transmission parameters of the ZnO nanorod based 64° YX LiNbO₃ SAW sensors before and after the deposition of the ZnO nanorod layer.
Fabricated bare 64° YX LiNbO₃ substrates show a resonant centre frequency peak at approximately 113 MHz with an insertion loss of approximately −7 to −8 dB. Deposition of ZnO seed and nanorod layers on a 64° YX LiNbO₃ substrate shift the resonance peak to 107 MHz without any significant variation in insertion loss. However, the resonant centre frequency has two sub peaks after deposition of the layers. The operational frequency of the sensor was found to be approximately 107.5 MHz in dry synthetic air at room temperature.

**Gas Sensing Results**

The hydrothermally grown ZnO nanorod based sensor was exposed to a hydrogen gas pulse sequence of 0.05%, 0.1%, 0.15% and 0.1% concentrations, a NO₂ gas pulse sequence of 0.42, 0.85, 1.27 and 0.85 ppm concentrations, and a CO gas pulse sequence of 50, 100, 150 and 50 ppm concentrations in synthetic air at operating temperatures between 200 and 300°C.

![Graph showing dynamic response of the sensor to different H₂ gas concentrations](image1.png)

*Figure 7.19: Dynamic response of the sensor to different H₂ gas concentrations in synthetic air at 265°C [13].*

![Graph showing frequency shift (kHz) versus H₂ gas concentration (%)](image2.png)

*Figure 7.20: Frequency shift (kHz) versus H₂ gas concentration (%) in synthetic air at 265°C [13].*
Figure 7.21: Dynamic response of the sensor to different CO gas concentrations in synthetic air at 265°C.

Figure 7.22: Frequency shift versus CO concentration (ppm).

Figure 7.23: Dynamic response of the sensor to different NO\textsubscript{2} gas concentrations in synthetic air at 265°C.

Like ZnO nanobelt based sensors, the ZnO nanorod based sensors also require an elevated operating temperature to enhance chemisorption of oxygen species to achieve the optimum
sensitivity. The optimal operating temperature of the ZnO nanorod based devices for H₂, NO₂ and CO sensing was found to be same at 265°C. The operational frequency of the sensor was found to be approximately 106.9 MHz in dry synthetic air at 265°C. Dynamic response of the ZnO nanorod based sensor towards different concentrations of H₂, NO₂ and CO at 265°C is shown in Figs. 7.19, 7.20 and 7.21, respectively. The measured responses were 274 kHz towards 0.15% of H₂, 266 kHz towards 425 ppb of NO₂ and 185 kHz towards 150 ppm of CO at 265°C. At 265°C, the 90% response and recovery time of the sensor were measured to be 28 and 36 sec for 0.15% of H₂, 16 and 24 sec for 425 ppb of NO₂ and 20 and 32 sec for 150 ppm of CO, respectively. It is noted that compared to commercial gas sensors, faster response and recovery were observed for the ZnO nanorod based SAW sensor.

Figure 7.24: Frequency shift (kHz) versus NO₂ concentrations in synthetic air at 265°C.

Figure 7.25: Frequency shift (kHz) versus operating temperature for 0.15% H₂, 425 ppb NO₂ and 150 ppm CO concentrations in synthetic air.

The response magnitude variation for the sensor to different H₂, NO₂ and CO concentrations is shown in Figs. 7.22, 7.23 and 7.24, respectively. Frequency shift increases almost linearly with the increase of H₂ concentration. However, the frequency shift increases non-linearly
with the increase of NO₂ and CO concentrations. Frequency shift versus operating temperature for 0.15% H₂, 425 ppb of NO₂ and 150 ppm of CO is shown in Fig. 7.25. It was found that the sensor responded with highest frequency shift towards H₂, NO₂ and CO gases at 265°C and at this temperature, a stable baseline frequency was also observed.

Short term reproducibility was observed as indicated when a second pulse of 0.1% H₂, 50 ppm CO and 850 ppb NO₂ was introduced into the sensor chamber. It was found that the ZnO nanorod based sensor produced repeatable responses of the same magnitude with a stable baseline.

The sensing mechanism is based on the reactions which occur at the sensor surface between the surface of nanorods and the gas molecules to be detected. In an air environment, oxygen molecules adsorb onto the surface of the ZnO nanorod layer to form O²⁻, O⁻, O₂⁻ ions depending on temperature by extracting electrons from the conduction band [6]. Since ZnO nanorods have single crystalline structure with average thickness less than 90 nm, adsorbed oxygen can easily penetrate through the bulk of the rod. The positively charged surface state and negatively charged adsorbed oxygen ions form a depletion region at the surface. Reducing gases such as H₂ and CO are oxidized to H₂O and CO₂, respectively consuming chemisorbed oxygen from the sensor surface by releasing electrons into the conduction band. This mechanism results in a reduction of surface depletion region to increase the film conductivity which corresponds to the gas concentration.

When an n-type ZnO nanorod surface is exposed to an oxidizing gas such as NO₂ at elevated temperatures, NO₂ molecules consume conduction electrons and subsequently increase the depletion region at the surface. Thus, ZnO nanorod layer conductivity is reduced after exposure to NO₂.

The particle or grain size of a conventional zinc oxide gas sensor is considerably greater than the depth of the surface space charge region, thus, electrical conduction is controlled by the grain boundaries. However, as synthesized ZnO nanorods have greatly reduced symmetrical hexagonal faces (average diameter 90 nm) whose dimensions are comparable to the depletion layer depth. Under these conditions, oxygen adsorption to the nanorods will lead to a complete depletion of conduction-band electrons with a large variation in resistance [12]. A schematic representation of physical and band model for nanorods based oxide surface and the film porosity is presented in Figure 2.5 and 2.6 in Chapter 2. The band model shows potential barriers formed at nanorod contacts and this barrier potential varies with the amount of adsorbed oxygen. It should be noted that this barrier potential is much higher than conventional inter-grain potential barriers due to a complete depletion of electrons in
nanorods. Thus the scale of conductivity modulation in nanorods is much greater than conventional ZnO grains after exposure to gases. The structural characterisation of the ZnO nanorods in Chapter 6 has provided crucial information about the nanorod morphology on the films. The promising gas sensing results of the nanorod based sensors prove that they have the potential for highly sensitive commercial gas sensing applications.

7.3.4 Sol-gel Prepared TiO$_2$ Nanoparticle Based SAW Sensor

**Frequency and Phase Response**

Figure 7.26 shows the measured S$_{21}$ transmission parameters of the TiO$_2$ and TiO$_2$-Au based 64° YX LiNbO$_3$ SAW sensors before and after the deposition of Au-doped TiO$_2$ nanoparticle layer. It was observed that the bare 64° YX LiNbO$_3$ substrate has a resonant centre frequency peak at approximately 113 MHz with an insertion loss of approximately −7.5 dB. Deposition of TiO$_2$ and TiO$_2$-Au layers on a 64° YX LiNbO$_3$ substrate shifted the resonance peak to 106 MHz with an insertion loss of approximately −16 dB. Addition of gold nanoparticles on the film slightly decreased resonant centre frequency and increased insertion loss. Stability of the phase responses was still good after deposition of the layers. The operational frequency of the sensor was found to be approximately 105 MHz in dry synthetic air at room temperature.

![Graph showing frequency and phase response of TiO$_2$ and TiO$_2$-Au layers on 64° YX LiNbO$_3$.](image)

Figure 7.26: Frequency and phase response of the TiO$_2$ and gold doped TiO$_2$ layer on 64° YX LiNbO$_3$ in ambient conditions.
Gas Sensing Results

The TiO$_2$ nanoparticles and Au-doped TiO$_2$ nanoparticles based SAW sensors were exposed to a hydrogen gas pulse sequence of 0.06%, 0.12%, 0.25%, 0.50%, 1%, and 0.12% concentrations in synthetic air at various temperatures between 150°C and 310°C. Gas exposure time was fixed at 6 mins for each pulse of H$_2$ gas and the cell was purged with synthetic air for 8 mins between each pulse.

The dynamic responses of TiO$_2$ and TiO$_2$-Au sensors to a sequence of different H$_2$ concentrations in synthetic air are shown in Figs. 7.27 and 7.28, respectively. The introduction of H$_2$ gas to the sensor surface causes an increase in the device’s resonant frequency for both of the sensors. With hydrogen exposure, the conductivity of the TiO$_2$ and TiO$_2$-Au layers decreases resulting in an increase in the acoustic wave velocity, thereby increasing the resonant frequency. The measured sensor response was approximately 6.5 and 7.4 kHz towards 1% of H$_2$ at 230°C for the TiO$_2$ and Au-TiO$_2$ sensors, respectively.

![Figure 7.27: Dynamic response of a TiO$_2$ based 64° YX LiNbO$_3$ SAW sensor towards H$_2$ at 230°C.](image)

![Figure 7.28: Dynamic response of a TiO$_2$-Au based 64° YX LiNbO$_3$ SAW sensor towards H$_2$ at 230°C.](image)
Chapter 7

The frequency shift (sensitivity) as a function of the operating temperature in the presence of 1% H₂ for both of the sensors is shown in Fig. 7.29. Gold doping increases the device sensitivity, and reduces the optimal operating temperature. The optimum operating temperatures for the TiO₂ based sensor are in the range of 245-260°C and for TiO₂-Au based sensor are in the range of 230-245°C. Both sensors exhibited reproducible responses and consistent baseline stability, as indicated when a second pulse of 0.12% hydrogen was introduced into the sensor chamber.

The gas sensing mechanism is governed by the reaction switch that occurs at the surface between the TiO₂ nanoparticles and gas molecules. It involves chemisorption of oxygen on the particle surface followed by charge transfer during the reaction of chemisorbed oxygen with target gas molecules [7] which is similar to sensing mechanism in ZnO as mentioned earlier. In air, oxygen molecules adsorb onto the surface of the TiO₂ layer in several forms such as: O₂⁻, O⁻ and O²⁻ depending on the operational temperature and form a depletion region at the oxide surface [7, 8]. This reduces the film conductivity. The addition of a reducing gas such as H₂ increases the film conductivity when the metal oxide is n-type and decreases the film conductivity when the metal oxide is p-type. It is evident from test results (Fig. 7.29) that gold nanoparticle addition to the TiO₂ has increased the sensor response towards H₂ by 1 kHz and decreased optimum operational temperature approximately 15°C. It is therefore supposed that the Au nanoparticles have an enhancing effect on the catalytic activity of TiO₂ for H₂ sensing in SAW device.

The mean diameter of grains or crystallites in metal oxides greatly influences gas sensing properties. It has been shown that sensor sensitivity increases with decreasing grain size [12]. Sol-gel prepared gold-doped TiO₂ film contains gold nanoparticles distributed on the surface having 10 nm average diameters. The film has 37% porosity. The characterisation results in
Chapter 6 that provide film properties and gas sensing results suggest that gold doping to the TiO$_2$ nanoparticles film has improved film sensing performance.

### 7.3.5 Polyaniline Nanofiber Based SAW Sensor

**Frequency and Phase Response**

Figure 7.30 shows the measured $S_{21}$ transmission parameters of the HCl and CSA doped polyaniline nanofiber based 64° YX LiNbO$_3$ SAW sensors before and after the deposition of polyaniline nanofiber layers. Fabricated 64° YX LiNbO$_3$ substrates have a resonant centre frequency peak at approximately 113 MHz with an insertion loss of approximately $-7$ to $-8$ dB. Deposition of an intermediate ZnO layer on a 64° YX LiNbO$_3$ substrate shifts the resonance peak to 108 MHz without any increase of insertion loss. Deposition of polyaniline nanofiber layers on a ZnO/64° YX LiNbO$_3$ substrate increased minimum insertion loss to approximately $-17$ dB without shifting the resonance peak. Both CSA and HCl doped nanofiber based films have the same resonant centre frequency, however CSA doped polyaniline nanofiber film has higher insertion loss than the HCl doped nanofiber film. Stability of the phase responses was still good after deposition of the layers. The operational frequency of both sensors was found to be approximately 108.2 MHz in dry synthetic air at room temperature.

![Frequency and Phase Response](image)

Figure 7.30: Frequency and phase response of the layered ZnO/64° YX LiNbO$_3$ substrate, and HCl and CSA doped polyaniline nanofiber layers on ZnO/64° YX LiNbO$_3$ in ambient conditions.
Gas Sensing Results

Hydrogen gas exposure time was arbitrarily fixed at 4 mins for HCl doped and 3 mins for CSA doped polyaniline nanofiber sensors, and the cell was purged with synthetic air for 8 mins for HCl doped and 4 mins for CSA doped sensors between each pulse of H₂ gas to allow the surface of the sensor to recover to atmospheric conditions. The HCl doped sensor was exposed to a hydrogen gas pulse sequence of 0.06%, 0.125%, 0.25%, 0.50%, 1%, and 0.06% concentrations and the CSA doped sensor was exposed to H₂ a hydrogen gas pulse sequence of 0.06%, 0.125%, 0.25%, 0.50%, 1%, and 0.125% in synthetic air at room temperature. The experimental set-up and testing procedures were outlined in details in section 7.2.

Figure 7.31: Dynamic response of HCl doped polyaniline nanofiber based ZnO/64° YX LiNbO₃ SAW sensor towards H₂ at room temperature [14].

Figure 7.32: Dynamic response of a CSA doped polyaniline nanofiber based ZnO/64° YX LiNbO₃ SAW sensor towards H₂ at room temperature [14].
The dynamic responses of the HCl doped and CSA doped polyaniline nanofiber sensors to different H\textsubscript{2} concentrations are shown in Fig. 7.31 and Fig. 7.32, respectively. The introduction of H\textsubscript{2} gas to the sensor surface causes reduction of the device’s resonant frequency for both of the sensors. With hydrogen exposure, the conductivity of the polyaniline nanofiber layer increases resulting in a decrease in the acoustic wave velocity, thereby decreasing the resonant frequency. The results are similar to those obtained by the authors for conductometric measurements on identical HCl doped conductometric sensors. Due to this similarity, the high electromechanical coupling coefficient of LiNbO\textsubscript{3}, and the low molecular weight of H\textsubscript{2} molecules, it is assumed that the conductivity change is more significant than the mass change.

The mechanism for the conductivity change in polyaniline due to interaction with hydrogen is still unclear. The SAW device results, and a separate measurement of resistivity, show that
resistance decreases in doped polyaniline on exposure to H₂. The hydrogen may form a bridge between nitrogen atoms on two adjacent chains or there may be partial protonation of some of the imine nitrogens [15]. It has also been suggested that the resistance change is caused by the formation of water [16].

The measured sensor responses are 3 kHz and 14.6 kHz towards 1% of H₂ for HCl doped and CSA doped polyaniline nanofiber sensors, respectively. The response magnitude variation for both sensors to different H₂ concentrations is shown in Fig. 7.33. The frequency shift increases non-linearly with the increase of H₂ concentrations for both of the sensors, saturating for large concentrations. The sensitivity of the 50 nm diameter CSA doped nanofiber sensors is greater than that of the 30 nm diameter HCl doped sensors, particularly for higher H₂ concentration.

The 90% response and recovery time of the sensors are shown in Fig. 7.34. Fast response and recovery are observed for both of the sensors. With increasing H₂ concentrations, response time decreases and recovery time increases for both sensors. However, the HCl doped sensor has faster response and recovery compared to the CSA doped sensor for all concentrations of H₂. This is consistent with the NH₃ sensing results of Liu et al. [17], who showed that the response time of polyaniline nanowire based sensors with various diameters corresponds to the radius-dependent diffusion time of ammonia gas into the wires.

Three factors may affect the differences observed with HCl and CSA synthesized doped polyaniline nanofibers: 1) the diameter of the nanofibers provide a differing amount of surface area for the H₂ to interact with; 2) differences in volatility and mobility of the dopants may cause variable speeds of reaction; and 3) there may be variation in the doping level of the dried films.

1) The diameters of the HCl doped nanofibers are approximately three-fifths that of the CSA doped nanofibers. This could play a role in the observed differences in sensitivity and response and recovery of the sensors. The faster response and recovery of the HCl doped sensor can be explained by faster adsorption of H₂. The decrease in sensitivity could be explained by faster gas penetration into the fiber. The higher surface area of the HCl doped nanofibers allows gas molecules to penetrate the fibers quickly so there is less delay in reaction time and saturation.

2) Since HCl is a small and volatile dopant it may be more mobile than bulky CSA, a non-volatile organic dopant. The mobility difference may increase the speed of interaction with H₂, but with the disadvantage of having less stable devices over long periods of
time. We observed increased stability of the baseline frequency with CSA doped polyaniline nanofibers versus the HCl doped nanofibers. The latter slightly increased in frequency over several weeks. This may be attributed to the volatility of HCl.

3) Slight variations in the purification can change the number of undoped imine nitrogens between the CSA and HCl doped polyaniline films. This can cause saturation differences with either a doping mechanism or a chain to chain interaction mechanism.

Reproducibility was examined by introducing a second pulse of 0.06% H$_2$ for the HCl doped nanofiber film and 0.125% H$_2$ for the CSA doped nanofiber film, into the sensor chamber. It was found that the polyaniline nanofiber based sensors produce repeatable responses of the same magnitude with good baseline stability.

**Effects of Nanofiber Based Film Thickness on the SAW Sensor’s Sensitivity**

The sensitivity of conventional polyaniline thin film gas sensors depends on the film thickness [18]. Generally, sensor sensitivity increases with a reduction of film thickness as the entire thickness of the film is affected by the reactions with gas species in a short period of time. For conductometric polyaniline nanofiber sensors, Kaner et al. [18] reported that the sensitivity is independent of film thickness in the range of 0.2-2 μm. Polyaniline nanofibers have a cylindrical morphology and form porous structures when deposited as thin films. Thus, sensitivity of a polyaniline nanofiber sensor is independent of film thickness, due to the porous structure of the film which leads to surface phenomena dominating the material response. Therefore, even in thicker films, all the fibers contribute to the sensing process as shown in Figure 2.2 in Chapter 2. This advantage allows the fabrication of sensors with reproducible response that have a large tolerance to thickness variation [18].

The author has investigated sensitivity variation in SAW devices based on polyaniline nanofiber thin layers. At first, the author has chosen five identical 64° YX LiNbO$_3$ substrates from the same fabrication batch. Then, CSA doped polyaniline nanofiber layers were randomly drop cast onto the active area of the SAW devices. The sensors were then left to dry for one day in a clean environment. The thickness of the nanofiber films was measured using a profile meter and found that average film thickness is 0.6 μm with a thickness deviation of ± 400 nm. The sensitivity of these five devices towards different concentrations of H$_2$ are compared in Figure 7.35. Even though the nanofiber film thickness variation is 400 nm, the sensitivity variation is below 5%. The test results suggest that, similar to conductometric sensors, the sensitivity of the polyaniline nanofiber based SAW sensors is also independent of film layer thickness.
Figure 7.35: Sensitivity comparison of CSA doped polyaniline nanofiber sensors when randomly drop-cast over five SAW substrates. Average thickness variation of the films is ±0.4 µm.

7.3.6 Polyaniline Nanofiber Based SAW Sensor: Electrodeposition

Frequency and Phase Response

Figure 7.36: Frequency and phase response of the bare 64° YX LiNbO₃ SAW substrate and electro-polymerized polyaniline nanofiber layer on 64° YX LiNbO₃ in ambient conditions.

Figure 7.36 shows the measured S₂₁ transmission parameters of the electrochemically polymerised polyaniline nanofiber based 64° YX LiNbO₃ SAW sensor with and without the
nanofiber layer. Deposition of a polyaniline nanofiber layer on a 64° YX LiNbO₃ substrate has shifted the resonance peak to 112 MHz with an insertion loss of approximately -18 dB. Stability of the phase responses after deposition of the layer was as good as without the layer. The operational frequency of the sensor was found to be approximately 111.2 MHz in dry synthetic air at room temperature.

Gas Sensing Results

The electrochemically synthesized polyaniline nanofiber based SAW sensor was exposed to a hydrogen gas pulse sequence of 0.06%, 0.125%, 0.25%, 0.50%, 1%, and 0.125% concentrations in synthetic air at room temperature. Dynamic response to a sequence of different H₂ gas concentrations in synthetic air is shown in Fig. 7.37. Measured sensor response was approximately 6.2 kHz towards 0.125% of H₂ in synthetic air. A fast response of 8 sec and a recovery time of 120 sec with good repeatability were observed at room temperature. Fig. 7.38 shows the frequency shift vs H₂ concentrations. The frequency shift increases non-linearly with the increase of H₂ concentrations and was almost flat at large concentrations. The author believes the developed devices will be useful for low concentration H₂ sensing.

The electrochemically grown polyaniline nanofiber based sensor also responded with same frequency shift towards repeated H₂ pulses (0.125%) as shown in Figure 7.37. However baseline frequency was not as stable as chemically grown polyaniline nanofiber based sensors. Although sensitivity and short term stability (7 days) is better for chemically grown nanofiber based sensors, faster response was observed for the electrochemically grown nanofiber based sensor. Therefore, real field applications will determine the choice of sensor.

Figure 7.37: SEM image of polyaniline nanofibers grown onto a SAW substrate.
7.3.7 Polyaniline Nanofiber Based Conductometric Sensor

Doping Effect on the Conductometric Sensitivity

In this sub-section, the author will present H₂ gas sensing results of doped and dedoped polyaniline nanofiber based conductometric sensors. The investigation of the test results has revealed the doping effect on sensor conductometric sensitivity. In addition, the test results also justify conductometric gas sensitivity of the SAW devices based on polyaniline nanofibers.

Figure 7.38: Frequency shift (kHz) versus H₂ gas concentration (%) at room temperature.

Dynamic responses of the dedoped and doped polyaniline nanofiber sensors to H₂ gas at room temperature are shown in Fig. 7.39 and 7.40, respectively. It was observed that the conductivity of both doped and dedoped sensitive layers increase after exposure to H₂ gas. It is also observed that at high concentrations of H₂ (0.25%, 0.5% and 1%), fast conductivity

Figure 7.39: Dynamic response of the dedoped polyaniline nanofiber based conductometric sensor to different H₂ gas concentrations in synthetic air [19].
increases followed by a slow decrease of the conductivity for both of the sensors. The observations indicate that either more than one type of reaction site is available, or that a number of different reactions are possible. The results prove that the sensors are useful for detecting a low concentration range of H$_2$.

![Graph showing dynamic response of the sensor](image1)

Figure 7.40: Dynamic response of the doped polyaniline nanofiber based conductometric sensor to different H$_2$ gas concentrations in synthetic air [19].

![Graph showing sensitivity comparison](image2)

Figure 7.41: Sensitivity of doped and dedoped polyaniline nanofiber sensors towards different concentrations of H$_2$ in synthetic air [19].

The sensor sensitivity ($R_{\text{air}}/R_{\text{gas}}$) was calculated to be 1.11 for doped and 1.07 for dedoped polyaniline nanofiber sensors upon exposure to 1% of H$_2$ at room temperature. Fast responses of 32 seconds and 28 seconds were observed towards 1% H$_2$ for doped and dedoped sensors, respectively. Two significant observations were obtained from the tests. Firstly, the response curves show that the doped polyaniline nanofiber sensor is more sensitive than the dedoped sensor (Fig. 7.41). Secondly, the baseline of the dedoped nanofiber sensor was more stable than the doped sensor. Additionally, the dedoped nanofiber sensor
has better repeatability than the doped sensor. Repeatability and stability of the sensors were confirmed by testing the sensors continuously over a 7 day period. It is believed volatility of dopant acid HCl is responsible for instability of doped sensor.

Although, the hydrogen storage properties of conducting polymers are being actively studied, the mechanism for polymer and hydrogen interactions is still not fully understood. Cho et al. [20] reported 6-8% (wt) hydrogen storage in HCl doped polyaniline and polyppyrrole at room temperature. The authors attributed this unusual phenomenon to the combined effects of the molecular sieving and metallic properties of the conducting polymer. This result could not be reproduced by Panella et al. [21] and Huang et al. [22] observed a much lower hydrogen storage capacity of 1.44% (wt). The hydrogen may form a bridge between nitrogen atoms on two adjacent chains or there may be partial protonation of some imine nitrogen atoms [15]. These reactions lead to the protonation of polyaniline nitrogen atoms, resulting in more delocalized charge carriers (polarons and bipolarons) on the backbone for conduction, and an increase of the film conductivity. It has also been suggested that the resistance change is caused by the formation of water [16]. The effects of water on the conductivity of polyaniline are well known [23, 24] and it has been established from nuclear magnetic resonance (NMR) spectroscopy studies that presence of water molecules in the polyaniline facilitates the charge transfer in the polyaniline backbone leading to an increase in polymer’s conductivity. In the process of H₂ and polyaniline interaction, a proportion of the analyte is probably catalytically oxidized forming water, which decreases the resistance of the both doped and dedoped polyaniline.

**7.3.8 Polyaniline/Metal Oxide Nanocomposite Based SAW Sensor**

**Frequency and Phase Response**

Figure 7.42 shows the measured $S_{21}$ transmission parameters of the polyaniline/ metal oxide nanocomposite based layered ZnO/64° YX LiNbO$_3$ SAW sensors before and after the deposition of the polyaniline/metal oxide nanocomposites layers. It was observed that resonant centre frequency and insertion loss are almost same for polyaniline/In$_2$O$_3$ and polyaniline/WO$_3$ nanocomposites based layered ZnO/64° YX LiNbO$_3$ sensors at approximately 110 MHz and −7 dB, respectively. However, after deposition of the polyaniline/SnO$_2$ nanocomposite, the resonant centre frequency decreased significantly to 105 MHz and minimum insertion loss increased to 14 dB. Stability of the phase responses after deposition of the layers was as good as without the layer. For all of the three polyaniline/metal oxide nanocomposite based sensors, the operational frequency was found to be approximately 107.3 MHz in dry synthetic air at room temperature.
Figure 7.42: Frequency and phase response of the polyaniline/metal oxide nanocomposite/64° YX LiNbO₃ SAW substrates in ambient conditions.

**Gas Sensing Results: Polyaniline/In₂O₃ Nanocomposite Based Sensor**

Figure 7.43: Dynamic response of the SAW sensor towards different concentrations of H₂ at room temperature [25].
Figure 7.44: Dynamic response of the SAW sensor towards different concentrations of CO at room temperature [25].

Figure 7.45: Dynamic response of the SAW sensor towards different concentrations of NO₂ at room temperature [25].

The dynamic response of the polyaniline nanofiber/ In₂O₃ nanoparticles composite based SAW sensor to a sequence of different H₂, CO and NO₂ gas concentrations in synthetic air is shown in Figs. 7.43, 7.44, and 7.45, respectively. The measured sensor responses were approximately 11.0, 2.0 and 2.5 kHz towards 1% of H₂, 500 ppm CO and 2.12 ppm NO₂ in synthetic air, respectively. The 90% response times were 30, 24 and 30 s for H₂, CO and NO₂, respectively. The corresponding 90% recovery times were 40, 36 and 65 s. It was also observed that for all three gases, response was slower at low concentrations compared to high concentrations. As a result, at low concentrations, high gas exposure times are required to obtain readable responses (frequency shift).
Reproducibility was observed as indicated when a second pulse of 0.12% H₂, 125 ppm CO and 510 ppb NO₂ were introduced into the sensor chamber. It was found that the polyaniline/In₂O₃ nanofiber based sensor produced repeatable responses of the same magnitude with good baseline stability for H₂ and CO gases, but not for NO₂. It is inferred from the dynamic response curve of the 3 gases that the frequency shift increases almost linearly for the increase of H₂ concentration (Fig. 7.46) but for CO and NO₂, the frequency shifts vs gas concentration are non linear. For NO₂ gas, the sensor response was not repeatable and the baseline drifts downward. It was found that the sensor could not recover to the baseline, and at 4.25 and 8.5 ppm NO₂ concentrations, the sensor response magnitude is lower than that of at 2.12 ppm. It is believed that high concentrations of NO₂ gas are poisoning the nanocomposite film. This was confirmed by exposing the sensor to a single pulse of 8.5 ppm NO₂, where a response of 4.5 kHz was observed. The result proves that the device is useful to sense low concentrations of NO₂.

**Gas Sensing Results: Polyaniline/WO₃ Nanocomposite Based SAW Sensor**

Dynamic response to a sequence of different H₂ gas concentrations in synthetic air is shown in Fig. 7.47. Measured sensor response was approximately 7 kHz towards 1% of H₂ in synthetic air. The 90% response time of 40 sec and recovery time of 100 sec with good repeatability were observed at room temperature. The response magnitude variation for the sensor to different H₂ concentrations at room temperature is shown in Fig. 7.46. The frequency shift increases non-linearly with the increase of H₂ concentration and saturating for high concentrations. Although the polyaniline/WO₃ nanofiber based sensor is less
sensitive to H₂ than the polyaniline/In₂O₃ nanofiber based sensor, it is more stable. The sensor did not produce any meaningful response towards CO and NO₂ gas exposure.

Figure 7.47: Dynamic response of a polyaniline/WO₃ nanofiber composite based 64° YX LiNbO₃ SAW sensor towards H₂ at room temperature.

It was observed that the polyaniline/WO₃ nanofiber composite based sensor produced repeatable responses of the same magnitude with good baseline stability.

**Gas Sensing Results: Polyaniline/SnO₂ Nanocomposite Based SAW Sensor**

Figure 7.48: Dynamic response of a polyaniline/SnO₂ nanofiber based layered ZnO/64° YX LiNbO₃ SAW sensor towards H₂ at room temperature.

The dynamic response to a sequence of different H₂ gas concentrations in synthetic air is shown in Fig. 7.48. Measured sensor response was approximately 7 kHz towards 1% of H₂ in synthetic air. The 90% response time of 30 s and recovery time of 120 s with good repeatability were observed at room temperature. The response magnitude variation for the
sensor to different $\text{H}_2$ concentrations at room temperature is shown in Fig. 7.46. The frequency shift increases non-linearly with the increase of $\text{H}_2$ concentration and saturating for high concentrations. The sensor did not respond towards CO and NO$_2$ gas exposure.

It was found that the polyaniline/SnO$_2$ nanofiber composite based sensor does not produce repeatable responses and the recovery to baseline after exposure to analytes was also poor. For all of the above sensors, repeatability was confirmed by testing the sensor continuously over a 5 day period.

Characterisation results of three nanocomposite films in Chapter 6 found that the average diameter of polyaniline nanofibers is 90 nm and the average diameter of the metal oxide nanoparticles is 55, 20, 25 nm for In$_2$O$_3$, WO$_3$, and SnO$_2$, respectively. For all cases, the nanofibers on the thin films are connected together in a network and the nanoparticles are embedded in the polyaniline nanofiber matrix. However, nanoparticle cluster formation was observed for WO$_3$ and SnO$_2$ composites. The gas sensing results in this chapter revealed that out of the three nanocomposite based sensors, polyaniline/In$_2$O$_3$ is the best in terms of sensitivity to $\text{H}_2$, NO$_2$ and CO gases. It is believed cluster formation of WO$_3$ and SnO$_2$ on the film is detrimental to sensor sensitivity as fewer particles are able to react with the analyte molecules.

**Gas Sensing Mechanism**

The mechanisms of hydrogen interaction with metal oxides are well known. Hydrogen is a reducing agent for the n-type metal oxide nanoparticles, increasing its conductivity on interaction. During the interaction process, the analyte dissociates on the surface of the metal oxide by injecting electrons. These free electrons reduce the surface depletion region, and thereby increase the surface conductivity. However, the mechanism for polyaniline and $\text{H}_2$ interactions is still unclear. Our previous experimental results [14] show that conductivity of polyaniline increases on exposure to $\text{H}_2$. The hydrogen may form a bridge between nitrogen atoms on two adjacent chains or there may be partial protonation of some of the imine nitrogens [15]. It has also been suggested that the change in resistance is caused by the formation of water [16].

The gas sensing mechanisms of the polyaniline/metal oxide nanocomposite are not yet understood, however we propose three possible mechanisms for the $\text{H}_2$ gas interaction. The first one is activation of the hydrogen by metal oxide due to formation of metal (indium/tungsten/tin)-dihydrogen complexes. The second one is an interaction with the polyaniline backbone, possibly facilitated by metal oxide (In$_2$O$_3$/WO$_3$/SnO$_2$) which may
induce dissociation of the hydrogen leading to either a doping type response or chain alignment. The third one is due to the closer packing of polyaniline backbones by metal oxide, and thus dissociation of the hydrogen molecule is stimulated by interaction with free spin on adjacent polyaniline chains.

The increase of the nanocomposite conductivity upon exposure to CO can be similarly described as conductivity increases due to interaction of polyaniline with CO [26-27]. A plausible sensing mechanism involves activation of CO, which is helped by \( \text{In}_2\text{O}_3 \) nanoparticles, to form \( \text{C}^+\equiv\text{O}^- \). This facilitates \( \text{C}^+ \) conjugation with the amine nitrogens \( (\text{HN}^\bullet\rangle \) of polyaniline. The conjugation results in polaronic forms \( (\text{HN}^{\bullet\bullet} \rangle \) in amine sites which increases the charge mobility on the polyaniline. The formation of a polaron could then be responsible for the increase in conductivity observed after exposure to CO.

The conductivity of a polyaniline/\( \text{In}_2\text{O}_3 \) film also increases with NO\(_2\) exposure, which indicates that this gas acts as a dopant for the composite. Polyaniline and \( \text{In}_2\text{O}_3 \) may form a p-n junction with a depletion region. Exposure to NO\(_2\) may cause reduction of the depletion region and hence increase the nanocomposite conductivity [28].

The sensors were tested in dry air. The results reported by other authors [16, 29-31] would suggest that humidity has a significant effect on the operation of the sensor presented here. This effect could be due to a combination of the conductivity change of the polyaniline layer or the adsorbed water on the surface of nanofibers.

Although the developed gas sensor is promising, low selectivity and lack of long term stability are of concern. There are several approaches to reduce these limitations, such as the use of catalysts and promoters, multi-sensor array systems and intelligent signal processing.

### 7.4 Summary

In this chapter, the gas sensing system, set-up and techniques employed by the author at RMIT University, Australia for electrical characterisation of the nanostructured material based SAW and conductometric sensors were highlighted, then the gas sensing performance of the nanostructured material based SAW and conductometric structures presented. To test the developed sensors the author employed a 4-channel gas calibration system which is capable of controlling a four component gas mixture by volumetric mixing of analytes. The system consists of both hardware and software components to autonomously control the experimental setup and log sensor test data from the output equipments.
ZnO nanobelts, ZnO nanorods, TiO$_2$ nanoparticles, polyaniline nanofibers, and polyaniline/metal oxide nanocomposites based sensors have been developed and investigated towards H$_2$, NO$_2$, and CO sensing applications. Although gas sensing performances of nanostructured material based conductometric devices are reported in the literature, to the author’s best knowledge, author is the first to report nanostructured material based SAW devices for gas sensing applications. The author’s research has led to many novel outcomes and contributions to the body of knowledge in the field of semiconducting metal oxides, conducting polymers and organic/inorganic nanocomposite based sensors. These are:

1. The average thickness and width-to-thickness ratios of the thermally evaporated ZnO nanobelts are in the range of 10 to 30 nm and ~5 to 10, respectively. The highest sensitivity for these nanobelt based SAW sensors was observed at 185°C for H$_2$ and 160°C for NO$_2$ gas with response times of 240 sec and 200 sec and recovery times of 280 and 390 sec for H$_2$ and NO$_2$ respectively.

2. The average thickness and width of the RF sputtered ZnO nanobelts are 10 nm and 50 nm, respectively. The optimum operating temperatures for the nanobelt based conductometric sensor are in the range of 300-400°C for H$_2$, 300-350°C for NO$_2$ and 350-420°C for propene sensing. However, it was found that the sensor has fastest response and recovery with greater repeatability and baseline stability at operational temperatures of 385, 350 and 370°C for H$_2$, NO$_2$ and propene gas, respectively.

3. The average diameters of hydrothermally grown ZnO nanorods are around 90 nm on gold and 40 nm on LiNbO$_3$. The highest sensitivity of the nanorod based SAW sensors was observed at 265°C for H$_2$, NO$_2$ and CO gases with response times of 28, 16 and 20 sec and recovery times of 36, 24 and 32 sec for H$_2$, NO$_2$ and CO, respectively. The measured responses at 265°C were 274 kHz towards 0.15% of H$_2$, 266 kHz towards 425 ppb of NO$_2$, and 185 kHz towards 150 ppm of CO.

4. The gas sensing results of sol-gel prepared TiO$_2$ and Au-doped TiO$_2$ nanoparticles based SAW devices revealed that gold nanoparticle addition to TiO$_2$ increased the sensor response towards H$_2$ by 1 kHz and decreased the optimum operational temperature by approximately 15°C.

5. The average diameter of the chemically polymerized polyaniline nanofibers is about 30 nm when HCl is used as a dopant acid during synthesis, and about 50 nm, when CSA is used as the dopant acid during synthesis, with lengths up to several microns. A critical investigation on polyaniline nanofiber based SAW sensor response towards H$_2$ was presented and shown to depend on nanofiber diameters i.e. doping acids. The
sensitivity of CSA doped nanofiber sensors is greater than that of the HCl doped sensors, particularly for higher H₂ concentration. However, the HCl doped sensor has faster response and recovery compared to the CSA doped sensor for all concentrations of H₂.

6. The gas sensing results of the HCl doped and dedoped polyaniline nanofiber based conductometric sensors towards H₂ show that the doped polyaniline nanofiber sensor is more sensitive than the dedoped sensor and the baseline of the dedoped nanofiber sensor was more stable than for the doped sensor. Additionally, the dedoped nanofiber sensor has better repeatability than the doped sensor.

7. Chemical oxidative polymerization of aniline in the presence of metal oxide nanoparticles (In₂O₃/WO₃/SnO₂) was employed to synthesize polyaniline nanofiber/metal oxide nanoparticle composites. The gas sensing results of these nanocomposites based SAW sensors were investigated. Of the three sensors, the polyaniline/In₂O₃ nanocomposite sensor outperformed in terms of sensitivity and stability.

It is the author’s opinion that the ZnO nanorod based SAW structure is the best candidate for sub-ppm H₂, NO₂, and CO sensing applications compared to the other nanostructured metal oxide based SAW structures investigated throughout this research program. It is also the author’s opinion that for room temperature operation, the polyaniline/In₂O₃ nanocomposite based SAW structure is the best candidate for sub-ppm H₂, NO₂, and CO sensing applications compared to the other polyaniline/metal oxide nanocomposites based SAW structures. The experimental gas sensing results presented in this chapter along with the thin film structural characteristics presented in Chapter 7, have enabled the author to publish seven referred journal and six international conference proceeding articles. A full list of the author’s publications can be found in Appendix A.
REFERENCES


Chapter 8

Conclusions and Future Work

This PhD research program commenced with the aim of investigating novel nanostructured materials/surface acoustic wave (SAW) devices for gas sensing applications. To achieve this goal, the author has proposed and developed novel layered nanostructured materials/ZnO/SAW devices as highly sensitive gas sensors. To the best of the author’s knowledge, the proposed layered nanostructured metal oxides or conducting polymers/ZnO/SAW device configurations have not previously been reported for gas sensing applications. In this PhD program, the author also developed nanostructured material based conductometric sensors for further investigation.

At first, nanostructured ZnO (nanobelts, nanorods), TiO$_2$ (nanoparticles), polyaniline (nanofibers) and semi-conducting metal oxide and polyaniline nanocomposites have been synthesized and deposited onto the SAW and conductometric transducers to develop novel sensors. Then, nanostructural characterization of the sensor’s surface were performed using SEM, TEM and XRD techniques to understand the surface morphologies of the sensitive materials to better evaluate film suitability for gas sensing. In third stage, the developed sensors were tested towards various concentrations of H$_2$, NO$_2$ and CO gases. The electrical characterization of the sensors towards various gases was performed to obtain the static and
dynamic parameters of the sensors such as sensitivity, optimum operating temperature, response and recovery times and baseline stability. Not only has the author investigated the gas sensing potential of nanostructured materials based devices, he also studied their gas sensing mechanisms.

This thesis presents the evolution of the author’s PhD research, which can be summarised by the following points:

1. Synthesis of the nanostructured semiconducting metal oxides (ZnO nanobelts, ZnO nanorods and TiO$_2$ nanoparticles), conducting polymers (polyaniline nanofibers) and polyaniline nanofibers/semiconducting metal oxides (In$_2$O$_3$, WO$_3$, SnO$_2$) nanocomposites.

2. Design and fabrication of the layered nanomaterial/ZnO/36° YX LiTaO$_3$ and nanomaterial/ZnO/64° YX LiNbO$_3$ SAW and nanomaterial based conductometric structures.


In the following sections, the author will briefly summarise the major findings of this research and present his recommendations for future work.

### 8.1 Conclusions

A summary of the major outcomes of this research program can be summarized below:

- Thermally evaporated single crystal ZnO nanobelts with the typical thickness and width-to-thickness ratios in the range of 10 to 30 nm and ~5 to 10, respectively, have been synthesized. To the author’s best knowledge, for the first time using these nanomaterials, layered nanobelts/ZnO/64° YX LiNbO$_3$ and nanobelts/ZnO/36° YX LiTaO$_3$ SAW devices were successfully fabricated for gas sensing applications. The highest sensitivity was observed at 185°C for H$_2$ and 160°C for NO$_2$ gas with response times of 240 sec and 200 sec and recovery times of 280 and 390 sec for H$_2$ and NO$_2$, respectively.

- RF sputtered single crystal hexagonal structure of ZnO nanobelts with average thickness and width of about 10 nm and 50 nm, respectively, have been synthesized.
To the author’s best knowledge, RF sputtered ZnO nanobelt based conductometric devices were successfully fabricated for the first time for gas sensing applications. The optimum operating temperatures for the sensor are in the range of 300-400°C for H₂, 300-350°C for NO₂ and 350-420°C for propene sensing. However, it was found that the sensor has fastest response and recovery, with greater repeatability and baseline stability, at operational temperatures of 385, 350 and 370°C for H₂, NO₂ and propene gas, respectively.

- Hydrothermally grown ZnO nanorods with the diameters of around 100 and 40 nm on LiNbO₃ and Au (metallization for electrodes), respectively, were successfully fabricated on a layered ZnO/64° YX LiNbO₃ based SAW structure. The ZnO nanorods density and morphology were different on the metallised gold and bare LiNbO₃ surfaces. The nanorods were densely packed and vertically grown on top of gold IDTs. To the author’s best knowledge, the developed SAW device is investigated for gas sensing applications for the first time and presented in this thesis. The highest sensitivity was observed at 265°C for H₂, NO₂ and CO gases with response times of 28, 16 and 20 sec and recovery times of 36, 24 and 32 sec for H₂, NO₂ and CO, respectively. The measured responses at 265°C were 274 kHz towards 0.15% of H₂, 266 kHz towards 425 ppb of NO₂, and 185 kHz towards 150 ppm of CO. It was found that ZnO nanorod based SAW sensors outperformed ZnO nanobelt based sensors in terms of sensitivity, response and recovery times. Additionally, ZnO nanorod based sensors have lower optimum operational temperature to sense H₂, NO₂ and CO gas species than ZnO nanobelts due to the densely oriented single crystal morphology of the nanorod thin films.

- Highly porous TiO₂ and Au nanoparticles doped TiO₂ films have been deposited on 64° YX LiNbO₃ SAW transducers. Sol-gel prepared gold doped TiO₂ films contain distributed gold nanoparticles on the surface having 10 nm average diameters. The porosity of the TiO₂ film was found to be 37%. The effect of Au nanoparticle doping on the sensitivity and operating temperatures were obtained and presented in this thesis. The test results revealed that gold nanoparticle addition to TiO₂ has increased the sensor response towards H₂ by 1 kHz and decreased the optimum operational temperature approximately 15°C. It is therefore supposed that the Au nanoparticles have an enhancing effect on the catalytic activity of TiO₂ for H₂ sensing in the SAW device. The author believes, that out of the all nanostructured metal oxides, ZnO nanorod based SAW sensors have the highest potential for industrial applications due to their high sensitivity (266 kHz) at very low concentration (425 ppb) of gas (NO₂).
• Hydrochloric acid (HCl) and camphor sulfonic acid (CSA) doped polyaniline nanofibers with average diameter of 30 and 50 nm, respectively, were synthesized using the rapidly mixed reaction method. Layered polyaniline nanofiber/ZnO/64° YX LiNbO₃ devices were developed for gas sensing applications and for the first time nanofiber diameter has been linked to hydrogen gas responses. The sensitivity of CSA doped nanofiber sensors was greater than that of the HCl doped sensors, particularly for higher H₂ concentration. However, the HCl doped sensor had faster response and recovery compared to the CSA doped sensor for all concentrations of H₂.

• Polyaniline nanofiber based conductometric sapphire structures were also fabricated to determine whether SAW response is due to mass or conductivity change. In addition, to the author’s best knowledge, for the first time comparison between doped and dedoped nanofiber sensors responses have been investigated. The results show that the doped polyaniline nanofiber sensor is more sensitive than the dedoped sensor and the baseline of the dedoped nanofiber sensor was more stable than the doped sensor. Additionally, the dedoped nanofiber sensor has better repeatability than the doped sensor.

• Novel polyaniline nanofiber and metal oxide (In₂O₃, WO₃, and SnO₂) nanoparticles composites/ZnO/64° YX LiNbO₃ devices were fabricated and their gas sensing results presented in this thesis. The average diameter of polyaniline nanofibers is 90 nm and the average diameter of the metal oxide nanoparticles is 55, 20 and 25 nm for In₂O₃, WO₃, and SnO₂, respectively. The nanofibers were connected together in a porous network. The nanoparticles were embedded in the polyaniline nanofibers matrix. Nanoparticle cluster formation was observed for WO₃ and SnO₂ composites. Out of the three nanocomposite-based SAW sensors, the polyaniline/In₂O₃ nanocomposite sensor outperformed in terms of sensitivity and stability. The author believes, the developed polyaniline nanofiber/ZnO/SAW and polyaniline/In₂O₃ nanocomposite/SAW devices have high potential for room temperature environmental and industrial gas sensing applications.

The author successfully fulfilled his research objectives by developing highly sensitive nanostructured material/ZnO/SAW and nanostructured material based conductometric devices for gas sensing applications, in both ambient and elevated temperature operations. Consequently, the author's research program has resulted in a number of novel and significant contributions to the field of nanostructured semiconductive metal oxide and conducting polymer based sensors. From these accomplishments there have been several key outcomes, the results of which have been published in referred journals and presented at
international conferences. These include six first author and three co-authored publications in referred journals which include IEEE Sensor journals, Sensor and Actuators A: Physical, Nanotechnology, Sensor Letters, Synthetic Metals, Journal of Sensors and Thin Solid Films. The author’s work has also resulted in over thirteen publications in international conference proceedings. A complete list of publications by the author can be found in Appendix A. Furthermore, the author became a referee for the IEEE Sensors and Sensors and Actuators journals in the process of this PhD program.

8.2 Future Work

This thesis has presented advances in the field of nanostructured material/ZnO/SAW and nanostructured material based conductometric devices for gas sensing applications. Throughout the course of this research, several areas of interest, which have tremendous research potential, have been identified. In this section some proposals will be made for possible future development of the current research. Firstly, the author believes that one of the most important stages for the continuation of this research will be the development of single nanowire, nanorod, nanofiber or nanotube based sensors for sensing down to few ppb of gas concentrations. To fabricate a single nanowire, nanotube or nanofiber at the device level will be challenging, especially the contact resistance. Multiple nanowires, nanobelts, nanorods or nanotubes can be aligned on top of the IDT patterns to reduce the device failure rates. The author also believes that the long term stability problem in current sensor technology can be overcome by using 1D single or multiple nanostructures based sensors as they are less susceptible to crystallinity changes.

The author believes this work could be extended to investigate the gas sensing mechanism at the nanoscale using density functional theory (DFT) modelling. This atomistic simulation will provide details of the transport properties of the carriers in single nanostructures so the device can be accurately designed for maximum performance.

Transducer technologies such as SAW, QCM and conductometric are quite mature, so it is the author’s opinion that only incremental advancements are likely to occur in these areas. Thus, new developments which may have a significant impact in the sensor field will be the investigation of the sensitive material morphology. However, it will be worth investigating nanostructured materials on film bulk acoustic resonator (TFBAR) and other acoustic wave devices which have much higher operating frequencies (GHz range). The details of the TFBAR structure and its operating principle are given in Chapter 1, Section 1.2.1.1.
Appendix A

List of Author’s Publications

The following papers have been published based on the work undertaken in this thesis, in refereed international journals and in the proceedings of international conferences:

A.1 Refereed Journals


### A.2 Conference Papers


