



SYNTHESIS OF ZnO NANOSTRUCTURES FOR GAS SENSING APPLICATIONS

By

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TABLE OF CONTENTS

THESIS DECLARATION	ii
ACKNOWLEDGEMENT	iii
LIST OF TABLES	vii
LIST OF FIGURES	viii
LIST OF ABBREVIATIONS	xi
LIST OF SYMBOLS	xii
SINSTESIS STRUKTUR-STRUKTUR NANO ZnO UNTUK APLIKASI PENGESANAN GAS	xiii
ABSTRAK	xiii
ABSTRACT	xv
CHAPTER 1	1
BACKGROUND	1
1.1 Introduction	2
1.2 ZnO Properties and Applications	2
1.3 Problem Statements.....	6
1.4 Research Objectives	7
1.5 Research Scopes.....	8
1.5.1 Effect of Growth Solution Concentrations on the Morphology of ZnO Nanoflakes.....	8
1.5.2 Pd doped ZnO Nanorods for Room Temperature Hydrogen Sensing Applications	9
1.5.3 ZnO Nanorods for Ultrasensitive Detection of Acetone	10
1.6 Research Methodology.....	11
1.7 Thesis Organogram	14
CHAPTER 2	16
MORPHOLOGICAL, OPTICAL, AND RAMAN CHARACTERISTICS OF ZnO NANOFLAKES PREPARED VIA A SOL-GEL METHOD	16
2.1 Abstract	17
2.2 Introduction	17
2.3 Experimental	19
2.4 Results and discussion.....	20

2.5	Conclusion.....	29
CHAPTER 3.....		31
EFFECT OF DIFFERENT SEED SOLUTIONS ON THE MORPHOLOGY AND ELECTRO-OPTICAL PROPERTIES OF ZnO NANORODS		31
3.1	Abstract	32
3.2	Introduction	33
3.3	Experimental	34
3.3.1	Preparation of seed solutions	34
3.3.2	Synthesis of ZnO-nanorods	35
3.3.3	Characterization of nanostructured ZnO.....	35
3.4	Results and Discussion.....	36
3.5	Conclusion.....	44
CHAPTER 4.....		45
MORPHOLOGICAL, STRUCTURAL, AND ELECTRICAL CHARACTERIZATION OF SOL-GEL-SYNTHESIZED ZnO NANORODS		45
4.1	Abstract	46
4.2	Introduction	46
4.3	Experimental	48
4.4	Results and Discussion.....	50
4.5	Conclusion.....	62
CHAPTER 5.....		63
SOL-GEL SYNTHESIS OF Pd DOPED ZnO NANORODS FOR ROOM TEMPERATURE HYDROGEN SENSING APPLICATIONS		63
5.1	Abstract	64
5.2	Introduction	64
5.3	Experimental	66
5.4	Results and discussion.....	68
5.5	Conclusion.....	77
CHAPTER 6.....		78
IMPACT OF HYDROGEN CONCENTRATIONS ON THE IMPEDANCE SPECTROSCOPIC BEHAVIOR OF Pd SENSITIZED ZnO NANORODS		78
6.1	Abstract	79
6.2	Introduction	79
6.3	Experimental	83

6.4	Results and Discussion.....	86
6.5	Conclusions.....	98
CHAPTER 7.....		99
SOL-GEL SYNTHESIS OF ZnO NANORODS FOR ULTRASENSITIVE DETECTION OF ACETONE		99
7.1	Abstract.....	100
7.2	Introduction.....	100
7.3	Experimental.....	102
7.4	Results and discussion.....	103
7.5	Conclusion.....	111
CHAPTER 8.....		112
THESIS CONCLUSION AND RECOMMENDATION FOR.....		112
FUTURE WORKS.....		112
8.1	Introduction.....	113
8.2	Thesis Conclusion.....	113
8.3	Recommendation for Future Works.....	116
REFERENCES.....		118
APPENDIX A.....		137
LIST OF PUBLICATIONS INCLUDED IN THE THESIS		137
APPENDIX B.....		143
FRONT PAGES OF PUBLISHED PAPERS		143
PUBLISHED PAPER FROM CHAPTER 2.....		144
PUBLISHED PAPER FROM CHAPTER 3.....		145
PUBLISHED PAPER FROM CHAPTER 4.....		146
PUBLISHED PAPER FROM CHAPTER 5.....		147
PUBLISHED PAPER FROM CHAPTER 6.....		148
PUBLISHED PAPER FROM CHAPTER 7.....		149
PUBLISHED PAPER FOR UV SENSING.....		150
APPENDIX C: PATENT (PENDING).....		156
MULTIVOLUME GAS CHAMBER FOR GAS SENSING APPLICATIONS		156
APPENDIX D.....		159
PRODUCT EXHIBITED FROM THIS WORK		159

LIST OF TABLES

Table 3.1: The values of inter plane distance d (Å), lattice parameters (Å) and grain size D (Å).....	39
Table 4.1: The structural parameters of ZnO nanorods	52
Table 4.2: Calculated “a” and “c” lattice constants (Å) for the ZnO nanorods	53
Table 4.3: Energy gaps (E_g), calculated refractive indices of nanostructure ZnO using Ravindra, N. M. et. al., (1979), Herve, P.J. L., & Vandamme, L. K. J. (1995), and Ghosh, D. K. et. al., (1984), models corresponding to optical dielectric constant	57
Table 6.1: Modeled RC parameters for Pd-sensitized ZnO nanorods under different H_2 concentrations at room temperature.....	93
Table 7.1: The values of inter plane distance d (Å) and grain size (nm) at each point of XRD peak (hkl).....	106

LIST OF FIGURES

Figure 1.1: Schematic diagram of ZnO thin film deposition and nanostructured growth	11
Figure 1.2: Schematic diagram of effect of different seed solutions.....	12
Figure 1.3: Schematic diagram of Pd doped ZnO nanorods.....	13
Figure 2.1: SEM images of ZnO nanoflakes showing surface morphology at: (a) 12.5 mM,(b)50 mM, and (c)75 mM of precursor.	22
Figure 2.2: Raman spectra of ZnO nanoflakes: (a) between 100 and 700 cm^{-1} and (b) the magnified view showing the Raman shift near the 430- cm^{-1} region.	24
Figure 2.3: PL spectrum of ZnO nanoflakes at different levels of precursor.	27
Figure 3.1: SEM images showing the surface morphologies of ZnO-nanorods synthesized on KOH-based seed layer (a) and monoethanolamine-based seed layer (b). The cross-sectional view of the above nanostructured ZnO grown on KOH- and monoethanolamine-based seed layers are demonstrated in (c) and (d), respectively.	37
Figure 3.2: XRD spectra demonstrating crystal qualities of ZnO-nanorods synthesized on KOH-based seed layer (a) and monoethanolamine-based seed layer (b).	39
Figure 3.3: Raman spectra reflecting crystalline, structural and orientation profiles of ZnO-nanorods synthesized on KOH-based seed layer (a) and monoethanolamine-based seed layer (b).....	41
Figure 3.4: Photoluminescence spectra demonstrating optical properties of ZnO-nanorods synthesized on KOH-based seed layer (a) and monoethanolamine-based seed layer (b).....	42

Figure 3.5: I-V curves showing the electrical properties of ZnO-nanorods synthesized on KOH-based seed layer (a) and monoethanolamine-based seed layer (b).	44
Figure 4.1: XRD pattern of ZnO nanorods.	51
Figure 4.2: SEM image of ZnO nanorods.	54
Figure 4.3: Photoluminescence spectra of ZnO nanorods at room temperature.....	54
Figure 4.4: Current to voltage characteristics of ZnO nanorods under dark condition and different UV exposure times.	59
Figure 4.5: Log(<i>I</i>) versus voltage characteristic curves of ZnO nanorods.	60
Figure 4.6: Photocurrent versus time response of ZnO nanorods at room temperature.	61
Figure 5.1: (a) SEM image and (b) XRD pattern of Pd doped ZnO nanorods.	69
Figure 5.2: XPS spectra of Pd doped ZnO nanorods: (a) survey spectra, (b) Zn 2 <i>p</i> spectra and (c) the deconvolution spectra in Pd 3 <i>d</i> region.	71
Figure 5.3: (a) <i>I-V</i> profile and (b) sensitivity curve for Pd doped ZnO nanorods as a function of hydrogen concentrations at room temperature.	72
Figure 5.4: Base line for the RT <i>I-V</i> characteristics curve: (a) after 40 ppm, (b) after 100 ppm, (c) after 200 ppm, (d) after 300 ppm, and (e) after 360 ppm of hydrogen.	73
Figure 5.5: (a) The dynamic response and (b) repeatability curves for Pd doped ZnO nanorods as a function of hydrogen concentrations at 200 °C.....	74
Figure 5.6: <i>I-V</i> characteristics curve: (a) RT till 75 °C, (b) 100 °C- 300 °C with air and with 1% H ₂ gas.	75
Figure 6.1: Process flow for the fabrication of ZnO nanorods device.....	84

Figure 6.2: SEM image of Pd-sensitized ZnO nanorods.	86
Figure 6.3: XRD (a) and EDS (b) spectra of Pd-doped ZnO nanorods.....	87
Figure 6.4: XPS spectra of Pd-doped ZnO nanorods. (a) survey spectra, (b) Zn 2 <i>p</i> spectra, and (c) the deconvolution spectra in Pd 3 <i>d</i> region.	89
Figure 6.5: I-V curves of Pd-doped ZnO nanorods from RT to 300 °C.	91
Figure 6.6: Nyquist plot of Pd-doped ZnO nanorods as a function of different H ₂ concentrations at room temperature.....	92
Figure 6.7: Imaginary parts of impedance for Pd-doped ZnO nanorods under different H ₂ concentrations at room temperature.	95
Figure 6.8: Gain curve for Pd-sensitized ZnO nanorods as a function of different H ₂ concentrations at room temperature.....	96
Figure 7.1: FESEM images of ZnO nanorods at a resolution of (a) 1K and (b) 100K.	104
Figure 7.2: XRD pattern of ZnO nanorods.	105
Figure 7.3: PL spectrum of ZnO nanorods.	106
Figure 7.4: Schematic diagram of the in house designed experimental set-up.	107
Figure 7.5: ZnO nanorods under different concentrations of acetone (a) Sensitivity curve (b) and repeatability curve(c) at 325 °C.	110

LIST OF ABBREVIATIONS

a.u.	Arbitrary Unit
AC	Alternating Current
BOE	Buffered Oxide Etch
C_{gb}	Grain Boundary Capacitance
DC	Direct Current
DI	Deionized
EDX	Energy Dispersive X-ray analysis
E_g	Energy Bandgap
FWHM	Full-width Half Maximum
Hz	Hertz
IS	Impedance Spectroscopy
I-t	Current- Time
I-V	Current- Voltage
MFC	Mass Flow Controller
ml	Milli Liter
MSM	Metal-Semiconductor-Metal
mW	Milli Watt
n	Refractive Index
nm	Nanometer
Pd	Palladium
PdO	Palladium Oxide
PL	Photoluminescence
ppm	Parts Per Million
RCA	Radio Corporation of America
R_{gb}	Grain Boundary Resistance
rpm	Revolution Per Minute
scm	Standard Cubic Centimeter Per Minute
sec	Second
SEM	Scanning Electron Microscope
UV	Ultraviolet
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
ZnO	Zinc Oxide

LIST OF SYMBOLS

θ	X-ray Diffraction Angle
σ	Conductivity
Ω	Ohm

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SINTESSIS STRUKTUR-STRUKTUR NANO ZnO UNTUK APLIKASI PENGESANAN GAS

ABSTRAK

Penyelidikan ke atas teknologi nano telah menjadi semakin popular disebabkan oleh sifat-sifat fizikal, kimia, optik dan pemangkin yang unik berbanding dengan pual yang lain. Teknologi nano telah merevolusikan banyak sektor teknologi dan industri seperti tenaga, keselamatan makanan, sains persekitaran, sains perubatan dan alat perubatan, keselamatan tanah air, dan lain-lain lagi. Antara bahan-bahan semikonduktor II-VI, ZnO merupakan bahan yang unik dan berbeza dengan jurang jalur yang lebar (3,37eV) dan loncatan tenaga ikatan yang besar (60 meV) pada suhu bilik. Struktur-struktur nano ZnO telah menarik perhatian di kalangan penyelidik disebabkan dengan sifat-sifat khususnya seperti pergerakan elektron yang tinggi, kekonduksian haba yang tinggi, ketelusan yang baik, dan kesenangan untuk membuat jenis struktur nano yang berlainan. Objektif kajian ini adalah untuk mensintesis struktur-struktur nano ZnO yang berbeza dengan menggunakan kaedah sol-gel penyalutan dengan cara putaran yang rendah kosnya untuk aplikasi gas. Satu lapisan benih ZnO yang nipis telah disalutkan untuk penyediaan tapak perkembangan bagi pertumbuhan struktur-struktur nano ZnO. Ciri-ciri morfologi permukaan, struktur, optik dan sifat elektrik struktur-struktur nano ZnO yang telah disintesis, telah dikaji dengan menggunakan SEM, XRD, PL, Raman, XPS, dan meter sumber. Interdigitated elektrod dengan emas dan perak telah disejatkan secara haba ke atas permukaan struktur-struktur nano ZnO dengan menggunakan topeng bayangan keluli tahan karat. Penyelidikan kini berjaya menunjukkan penggunaan kaedah sol-gel untuk mensintesis struktur-struktur nano yang berbeza. Tambahan pula, ZnO yang direka berasaskan pengesanan nano juga telah digunakan untuk aplikasi pengesanan UV serta pengesanan gas. Dalam tesis ini, kita telah mempelajari kesan kepekatan-kepekatan molar bahan asas ke atas morfologi struktur-struktur nano ZnO. Ia telah diperhatikan bahawa rod-rod nano ZnO cenderung untuk tumbuh bersama-sama dengan serpihan-serpihan nano ZnO dan kepadatan rod-rod nano ZnO meningkat dengan peningkatan kepekatan molar daripada 0.05M ke 0.075M. Spektrum PL dan Raman juga menunjukkan pengalihan merah dan pengalihan merah ini disebabkan oleh pemanasan sendiri. Kesan pelarut yang berbeza untuk penyediaan larutan asas juga telah dikaji. Ia telah diperhatikan bahawa larutan benih yang berbeza sangat mempengaruhi arah pertumbuhan rod-rod nano ZnO serta kekonduksian peranti. Ia telah diperhatikan bahawa dengan pendedahan cahaya UV, semibulatan arka yang kedua yang menunjukkan proses elektrod telah dikurangkan. Kajian terperinci telah dijalankan untuk mengkaji kesan masa pendedahan UV terhadap kestabilan arus peranti dan ia telah diperhatikan bahawa selepas 60 minit pendedahan UV, aliran arus masih stabil telah diperhatikan. Penentuan kestabilan arus selepas pendedahan UV adalah penting untuk aplikasi pengesanan gas dan optoelektronik berasaskan UV. Akhirnya, kita telah memfabrikasi rod-rod nano ZnO yang telah

didopkan Pd dan ZnO yang tulen untuk aplikasi pengesan gas. Pengesan yang difabrikasikan telah berjaya diuji dengan kepekatan gas hydrogen dan aseton yang tinggi, iaitu masing-masing 40 ppm-360 ppm dan 0.05 ppm-457 ppm. Ia telah diperhatikan bahawa pengesan ini adalah sekurang-kurangnya 25 kali ganda lebih sensitif daripada rod-rod nano ZnO yang telah didopkan Pd yang didokumenkan untuk mengesan hydrogen pada suhu persekitaran bilik. Pengesan yang telah difabrikasikan menunjukkan penyusutan dalam rintangan sempadan butiran daripada 11.95 K Ω ke 3.765 K Ω apabila kepekatan hydrogen telah meningkat daripada 40 ppm ke 360 ppm. Pengesan aseton berasaskan rod-rod nano ZnO menunjukkan pengesan aseton yang cemerlang dalam pelbagai kepekatan aseton (0.05 ppm-457 ppm). Pengesan ini menunjukkan masa tindak balas dan masa pemulihan masing-masing dengan 8 s dan 428 s bagi 183 ppm aseton. Pengesan ini juga mempamerkan keboleholangan yang baik di bawah pendedahan 183 ppm aseton. Kesimpulannya, kajian ini telah berjaya menunjukkan proses untuk mensintesis, menfabrikasikan, menyifatkan dan menguji ZnO yang distruktur nano kan berasaskan pengesanan UV dan gas dengan menggunakan sol-gel penyalutan dengan cara putaran.

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SYNTHESIS OF ZnO NANOSTRUCTURES FOR GAS SENSING APPLICATIONS

ABSTRACT

Research on nanotechnology has become increasingly popular because of their unique physical, chemical, optical and catalytic properties compared to their bulk counterparts. Nanotechnology revolutionize many technology and industry sectors such as energy, food safety, environmental sciences, medical sciences and medical instrumentation, homeland security, and many others. Among II-VI semiconductor materials, ZnO is a unique and distinguish material with wide band-gap (3.37 eV) and the large exciton binding energy (60 meV) at room temperature. ZnO nanostructures have attracted great attention among the researchers due to its peculiar properties such as high electron mobility, high thermal conductivity, good transparency, and easiness to fabricate different type of nanostructures. The objective of this research is to synthesize different ZnO nanostructures using low-cost sol-gel spin coating method for gas sensing applications. A thin seed layer of ZnO was deposited to provide the nucleation sites for the growth of ZnO nanostructures. The surface morphology, structural, optical and electrical properties of the synthesized ZnO nanostructures was characterized using SEM, XRD, PL, Raman, XPS and sourcemeter. Gold and silver interdigitated electrodes were thermally evaporated on the surface of ZnO nanostructures using stainless steel shadow mask. The current research successfully demonstrated the application of sol-gel method to synthesize different nanostructures. Moreover, the fabricated ZnO based nano-sensors have also been applied for gas sensing applications. In this thesis, we have studied the effect of precursor molar concentrations (0.0125-0.075 M) on the morphology of ZnO nanostructures. It was observed that the ZnO nanorods tend to grow along with the ZnO nanoflakes and the density of ZnO nanorods increases as the molar concentrations increased from 0.05 M to 0.075 M. The PL and Raman spectra also redshifted and the redshifting were attributed due to local heating. The effect of different solvent for the seed solution preparation was also studied. It was observed that different seed solution greatly affects the growth direction of ZnO nanorods as well the conductivity of the device. The detailed study was conducted to investigate the effect of UV exposure time on the device current stability and it was observed that after 60 min of UV exposure a stable current flow was observed. The determination of stable current after UV exposure is important for UV-based gas sensing and optoelectronic applications. Finally, we fabricated the Pd-doped ZnO nanorods, and pure ZnO nanorods for gas sensing applications. The fabricated sensors were successfully tested for a wide range of hydrogen and acetone concentrations 40-360 ppm, and 0.05- 457 ppm, respectively. It was observed that the sensor was at least 25 fold more sensitive over the literature documented Pd-doped ZnO nanorods in detecting hydrogen at room ambient temperature. The fabricated sensor displayed the decrement in grain boundary resistance from 11.95 to 3.765 K Ω when the hydrogen concentration was increased from 40 to 360 ppm. The acetone sensor based on ZnO nanorods exhibited excellent acetone sensing over a wide range of acetone concentrations (0.05- 457 ppm). The sensor exhibited the response and recovery times of 8 s and 428 s, respectively, for 183 ppm of acetone. The sensor also displayed good repeatability under the exposure of 183 ppm of acetone.

CHAPTER 1

BACKGROUND

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BACKGROUND

1.1 Introduction

The purpose of this chapter is to provide a general framework and introduction for the work presented in the current thesis. This chapter is divided into five sections, addressing the ZnO properties and application, problem statement, research objectives, research scopes and thesis organogram.

1.2 ZnO Properties and Applications

Zinc oxide is a II-VI compound semiconductor material and it has been under intensive focused among the researchers because of its unique properties such as high electron mobility with undoped state, high thermal conductivity, good transparency, wide bandgap (~3.37 eV), large exciton binding energy (60 meV) which is much larger than that of GaN. Moreover, required a simple process for fabricating different nanostructures by adopting various techniques to make ZnO nanostructures suitable for optoelectronics and in UV sensors (Chang, H. et. al., 2011), chemical sensors (Umar, A. et. al., 2008), and hydrogen storage (Wan, Q. et. al., 2004), etc. The ZnO possess unique physical properties. The growth of ZnO nanostructures can be achieved using different low and high temperature growth methods. The most useful high temperature techniques used are metal organic chemical vapor deposition (MOCVD) and vapor liquid solid (VLS) (Hussain, I. et. al., 2011) and the sol-gel method is low temperature technique. ZnO nanorods and nanoporous are the most important nanostructures which offer additional advantages for light emission due to increased junction area, enhanced

polarization dependence of reflectivity and improved carrier confinement in one dimensional nanostructure (Chang, C.-Y. et. al., 2006; Bano, N. et. al., 2010).

Hydrogen is a non-toxic, non-poisonous, colorless, odorless and tasteless gas and cannot be detected by human senses. Hydrogen has a very low density (0.0899 kg/m^3) with a high diffusion coefficient ($0.61 \text{ cm}^2/\text{s}$ in air). The H_2 content in air at sea level is 0.5 ppm and has no threshold limit value (Schwandt, C., & Fray, D. J. 2000). Hydrogen can be ignited easily with a very small amount of energy, as small as 0.02 mJ (Zhang, P. 2008; Hübner, T. et. al., 2011). The explosive range is wide, from 4% to 75% (Al-Hardan, N. H. et. al., 2010). Monitoring of hydrogen concentration is essential to nuclear reactor safety (Hübner, T. et. al., 2011). In coal mines hydrogen can be produced in the ppm² range by methane or coal-dust explosions or by the spontaneous heating and low-temperature oxidation of coal (Brungs, M. et. al., 1992).

Hydrogen is an energy carrier and can contribute to overcoming the problems of dwindling fossil fuel reserves, energy supply security and global warming (Hübner, T. et. al., 2011). In 2006, 10638 thousand metric tons of H_2 was produced in the United States. Most of this H_2 was used in petrochemical plants, fertilizer plants (ammonia production) and the methanol industry (Korotcenkov, G. et. al., 2009), while a minuscule fraction of H_2 (50 tons in 2006) was used as an alternative fuel for electric power generation and transportation applications. This small fraction of H_2 used in power generation and transportation is growing rapidly, resulting in greater presence and distributed H_2 in society. In this emerging hydrogen economy the detection of hydrogen leaks and the measurement of hydrogen concentration are necessary during production, storage, transportation and use in both stationary and mobile applications (Hübner, T. et. al., 2011). Sensors will therefore be used for safety monitoring of

hydrogen production plants, pipelines, storage tanks, refueling stations and automotive vehicles (Hübert, T. et. al., 2011).

Alternative hydrogen detection methods employ instruments such as gas chromatographs, mass spectrometers or specific ionization gas pressure sensors. Traditionally, these instruments are relatively large, expensive, high maintenance, and slow in terms of their sampling and reaction times (Hübert, T. et. al., 2011). Therefore, the researchers have continued the investigation of various techniques to develop H₂ sensor with high sensitivity and fast response time. Hydrogen sensors have several advantages over the conventional hydrogen detection methods, including their low cost, smaller size and faster response (Hübert, T. et. al., 2011). These advantages make them more suitable for portable and in situ hydrogen detection in a range of applications (Hübert, T. et. al., 2011).

The commercially available sensors are primarily based on semiconductor metal oxides, electrochemical H₂ oxidation, catalytic response, thermal conductivity response or optical response technology. Although, these sensors are sensitive, and reliable, electrochemical based sensors suffers from decrease in sensitivity with time due to deterioration of the electrode catalyst; catalyst based sensors are not specific to H₂ and others need high temperature or high power for their operation. The most successful commercial sensors based on metal oxides are small in size, highly responsive, cheap and operate using a relatively simple electric circuit.

However, these sensors require a significant pre-heating of the sensing element (up to 300-700 °C) to achieve the desired sensitivity and accuracy (Aroutiounian, V. 2007; Yang, M. et. al., 2010; Lupan, O. et. al., 2010a; Aroutiounian, V. M. et. al., 2008; Katsuki, A., & Fukui, K. 1998). Recently, the main effort in H₂ sensor development using metal oxides focused on improving the sensitivity and decreasing the operating

temperature. In room temperature sensing ZnO has shown improved response and short recovery time due to its wide bandgap, surface adsorbed oxygen species and a cost effective, easy, fast and reproducible synthesis in nanostructured form.

Diabetes is a long life condition that may cause death and seriously affects the quality of life of a rapidly growing number of individuals (Righettoni, M., & Tricoli, A. 2011). The number of people suffering from diabetes (type- 1 and -2) is increasing due to population growth, aging, urbanization, and increasing occurrence of obesity and physical inactivity (Righettoni, M., & Tricoli, A. 2011; Wild, S. et. al., 2004). Acetone is a specific breath marker for type-1 diabetes (Righettoni, M., & Tricoli, A. 2011; Cao, W., & Duan, Y. 2007; Henderson, M. J. et. al., 1952) and its concentration increases from 300 to 900 ppb for healthy humans (Righettoni, M., & Tricoli, A. 2011; Diskin, A. M. et. al., 2003) to more than 1800 ppb (Righettoni, M. et. al., 2011; Deng, C. et. al., 2004) for diabetic patients. Moreover, several studies are suggesting that breath acetone concentration may be correlated with blood glucose levels and thus its monitoring has the potential to become a new standard insulin management (Righettoni, M., & Tricoli, A. 2011; Henderson, M. J. et. al., 1952; Sulway, M. J., & Malins, J. M. 1970).

Currently, breath acetone testing is carried out using gas chromatography followed by flame ionization detection (Righettoni, M., & Tricoli, A. 2011; Sanchez, J. M., & Sacks, R. D. 2003), ion mobility spectrometry (Lord, H. et. al., 2002) and MS detection (Phillips, M. et. al., 1999). These methods need bulky instrumentation and skilled operators. Sample collection and pre-concentration involves a laborious procedure before the introduction of the collected samples into a gas chromatograph column (Righettoni, M., & Tricoli, A. 2011). Furthermore, some or all of the breath acetone may be lost during these time consuming steps. Because of these limitations, these methods are not very suitable for use in diabetes diagnosis and acetone

monitoring outside the laboratory (Righettoni, M., & Tricoli, A. 2011). Alternative approaches proposed to detect gas traces in low concentrations include electrochemical sensor (Wang, C.-C et. al., 2007), surface acoustic wave (Penza, M. et. al., 2001), quartz crystal microbalance (Ying, Z. et. al., 2008; Huang, H. et. al., 2004; Young, D. J. et. al., 2009), and semiconductor gas sensors.

1.3 Problem Statements

Nanostructured ZnO can be synthesized using a number of methods including vapor solid (VS), vapor liquid solid (VLS), Radio Frequency (RF) sputtering and sol-gel. VS and VLS required high temperature for the growth of nanostructures. On the other hand, RF required expensive instruments and specialized laboratory setup. Moreover, in some of the cases the sensor fabrication step needs the addition of various dopants which are very complicated and time consuming. On the contrary, the sol-gel method is cost effective and can synthesize ZnO with controlled nanostructures, morphology and dopants. However, the sol-gel methods for the synthesis of nanostructure ZnO are not well characterized.

ZnO nanostructures in the form of one dimensional (1D), and two dimensional (2D) have high surface to volume ratios, making them useful for variety of applications (Usman Ali, S. M. et. al., 2011). Two dimensional (2D) ZnO nanostructures have been fabricated using various methods but the sol-gel hydrothermal method is the simplest one and allows the preparation of ZnO nanostructures at low temperature. In the reported literature (Cheng, J. P. et. al., 2008; Cheng, J. P. et. al., 2009), researchers utilized Al as a substrate to form the porous structure of ZnO nanoplates. Using Al as a substrate has some potential problems: (i) Al is quickly oxidized by atmospheric

oxygen, (ii) Al is a good conductor and therefore a thick layer of Al under the ZnO nanostructure might be problematic while applying in electrical devices.

For the room temperature hydrogen sensing applications researchers usually used Pd or Pt as a dopant source along with the ZnO nanorods. For the introduction of dopant or catalyst special equipment's are required. For the synthesis of ZnO nanorods the predominant methods are chemical vapor deposition and molecular beam epitaxy (Ren, S. et. al., 2011). However, both CVD and MBE methods involved high temperature growth and expensive instrumentation which are not available everywhere. Also these techniques required gold or other expensive metal coating for the synthesis of ZnO nanorods and nanowires. Moreover, the Pd doping onto the synthesized ZnO required RF sputtering which also needs expensive laboratory set-up. The other main issue in gas sensing is to detect the very low concentration of acetone. Because of getting low level acetone detection one can classify the state of diabetes without using expensive and time consuming equipment's (Righettoni, M., & Tricoli, A. 2011). Based on above mentioned issues, this research proposed alternative ways in order to minimize the cost and time. In order to resolve the above addressed issues, the current work was carried out and successfully demonstrated the alternative ways to resolve the current issues.

1.4 Research Objectives

The aim of this thesis is to synthesize and characterize ZnO nanostructures using sol-gel route for gas sensing applications. The research is accomplished using the following specific objectives:

- I. To determine the effect of various growth solution concentrations and different seed solutions on the structural, morphological, optical, and electrical properties of ZnO nanostructures.
- II. To fabricate and characterize the Pd doped ZnO nanorods sensor for room temperature hydrogen sensing applications.
- III. To synthesize and test the ZnO nanorods sensor for ultrasensitive detection of acetone.

1.5 Research Scopes

The research is embarked based on the following scopes:

1.5.1 Effect of Growth Solution Concentrations on the Morphology of ZnO Nanoflakes

Two dimensional ZnO nanostructures with a high surface to volume ratio are suggested to be ideal for the nanodevices used in energy storage and conversion (Cheng, J. P. et. al., 2009; Ma, M. et. al., 2008), chemical and biological sensors (Umar, A. et. al., 2008; Usman Ali, S. M. et. al., 2010), field emission (Bai, W. et. al., 2008; Chin, K. C. et. al., 2008) and photocatalytic degradation of organic dye (Cheng, J. P. et. al., 2009; Ye, C. et. al., 2006). However, studies regarding 2D nanostructures are less common compared those regarding 1D ZnO nanostructures (Cheng, J. P. et. al., 2009). Cheng, J. P. et. al., (2005), have reported an electrochemical method to grow vertically aligned ZnO nanoplates on Zn foil, where small variations in the electrochemical potential gave rise to a variety of crystal morphologies including 1D and 3D growth. Cheng, J. P. et. al., (2009); Hosono, E. et. al., (2004), have fabricated the oriented ZnO nanoplates on glass slide with layered hydroxide zinc acetate precursor for pyrolytic transformation. Cheng, J. P. et. al., (2009); Xu, F. et. al., (2007) reported a

hydrothermal procedure for high-yield synthesis of ZnO hexagonal nanoplates on Zn foil. Ye, C. et. al., (2006) reported ZnO nanoplates as thin as 10 nm on Al substrate that had higher efficiency in photodegrading organic dyes than ZnO nanorods did. However, so far there have been no reports on the effect of growth solution concentration on the morphology of ZnO nanostructures on thin Al coated silicon substrate. In this research, for the 1st time we studied the effect of different concentrations of growth solution on the morphology of ZnO nanostructures on thin film Al coated silicon substrate using low cost sol-gel spin coating method.

1.5.2 Pd doped ZnO Nanorods for Room Temperature Hydrogen Sensing Applications

Hydrogen is the most attractive and ultimate candidate for future fuel and energy carrier. Hydrogen does not require fuel processors in fuel cells, and is reproducible from renewable energy resources (Aroutiounian, V. (2007)). Monitoring of the hydrogen concentration is very important for the fuel cell applications, as well as in chemical industry. Among the various type of sensors, chemiresistor based hydrogen sensors have been studied due to their relatively simple structure and well-established detection mechanism (Zhang, P. 2008). This work has proposed the sol-gel synthesis of Pd doped ZnO nanorods for room temperature hydrogen sensing. The detailed study was carried out using ac impedance spectroscopy to investigate the sensing mechanism. The other part has proposed the sol-gel synthesis of ZnO nanorods for room temperature hydrogen sensing using DC measurements.