SYNTHESIS AND APPLICATION OF ZNO NANORODS FOR OXYGEN GAS SENSOR

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SYNTHESIS AND APPLICATION OF ZNO NANORODS FOR OXYGEN GAS SENSOR

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LIST OF SYMBOLS

R_{NW}	Nanowire resistance
ρ	Nanowire resistivity
L	Nanowire length
D	Nanowire radius
L_D	Width of depletion layer
E_C	Conduction band
E_V	Valence band
E_F	Fermi level
Δ_{air}	Thickness of the space charge
$eV_{surface}$	Potential barrier
e^-	Conduction electron
$^+$	Elementary charge of donor sites
G	Conductance of electron
η	Carrier concentration
e	Elementary charge
μ	Mobility of the carrier

S	Sensitivity
G_g	Nanorods conductance in oxygen gas
G_a	Nanorods conductance in ambient air
λ_D	Debye length
V_s	Interfacial potential
k	Boltzman constant
T	Temperature
N_d	Concentration of donor impurity
M	Molarity
P_v	Vapour pressure
P	Chamber pressure
R_{ZnO}	ZnO resistance
C_{di}	Dielectric capacitance
R_C	Electrode-ZnO contact resistance
R_{gi}	Average resistance of inter-grain boundary
R_l	Series resistance of depleted region of bulk ZnO
qV_s	Band bending of the surface layer
qV_c	Band bending induced at the electrode ZnO contact

Å	Angstrom
R_{air}	ZnO resistance in baseline oxygen gas in open environment
R_{gas}	ZnO resistance at targeted concentration
ΔR	Change of resistance
τ_{res}	Response time
τ_{rec}	Recovery time
δ_{time}	Time drift
$\hat{S}$	Compensated sensor signal
y	Measured response
x	Sensor response without drift
δ	Drift
δ_{θ}	Temperature drift coefficient
$\delta_{\emptyset}$	Relative humidity drift coefficient
δ_{t}	Time drift coefficient
N	Nucleation density
ΔG	Activation energy of nucleation
ΔG_{V}	Volume free energy
ΔG_{s}	Surface free energy

SINTESIS DAN APPLIKASI NANOROD ZnO UNTUK PENDERIA GAS OKSIGEN

ABSTRAK

Di dalam tesis ini, penderia gas oksigen dengan kepekaan dan ketepatan yang tinggi pada suhu operasi di suhu bilik telah berjaya dibangunkan menggunakan nanorod *ZnO*. Satu siri kajian melalui *hydrothermal* dan *PECVD* telah dijalankan bertujuan untuk menghasilkan nanorod ZnO yang mempunyai kepadatan dan nisbah aspek yang tinggi. Kajian menunjukkan bahawa nanorod ZnO dengan kepadatan yang tinggi dan mempunyai nisbah aspek 15:1 boleh dihasilkan pada suhu penyepuhlindapan 100^{o}C dengan masa pertumbuhan 3 jam untuk kaedah *hydrothermal*. Manakala untuk *PECVD*, nanorod ZnO dengan nisbah aspek 12:1 berjaya dihasilkan menggunakan pemangkin emas setebal 4 nm di dalam bekas dengan tekanan 700 mTorr. Analisis dari *SEM* dan *AFM* menunjukkan formasi nanorod ZnO melalui *hydrothermal* dipengaruhi oleh morfologi partikel benih manakala untuk *PECVD*, saiz partikel Au dalam skala nano dan campuran nisbah yang betul antara komponen prekursor merupakan parameter utama yang memberi kesan terhadap pertumbuhan nanorod ZnO. Nanorod ZnO yang dihasilkan dari kedua-dua kaedah ini merupakan jenis kristal wurtzite berdasarkan ukuran anjak raman pada mod E_2(tinggi), 436cm^{-1}. Pencirian elektrik menggunakkan empat titik prob telah dijalankan dan keputusan menunjukkan sifat hakiki rintangan elektrik untuk nanorod ZnO yang dihasilkan melalui *hydrothermal* dan *PECVD* masing-masing ialah $4.47 \times 10^{-3} \Omega.cm$ dan $47 \times$

$10^{-3}\Omega.cm$. Kepekaan terhadap gas oksigen untuk kedua-dua nanorod ZnO telah dibandingkan di dalam suasana ambien dan keputusan menunjukkan nanorod ZnO yang dihasilkan melalui *hydrothermal* adalah lebih peka dengan perubahan rintangan sebanyak 57.67%. Keputusan juga menunjukkan kepekaan penderia gas telah meningkat dengan berkurangnya saiz nanorod ZnO. Masa tindak-balas, kebolehupayaan memilih, resolusi, kestabilan, kesan suhu dan kesan kelembapan terhadap penderia juga telah diperincikan. Kehanyutan isyarat penderia terhadap perubahan suhu, kelembapan dan masa di dalam suasana sebenar telah berjaya diimbangkan melalui kaedah manipulasi garis dasar dan keputusan menunjukkan penderia mempunyai ketepatan setinggi 99.5% apabila dibandingkan dengan penderia yang komersial.

SYNTHESIS AND APPLICATION OF ZnO NANORODS FOR OXYGEN GAS SENSOR

ABSTRACT

In this thesis, a high sensitivity and accurate gas sensor with operating temperature at room temperature has been successfully developed by using ZnO nanorods. A series of parametric studies via hydrothermal and PECVD have been carried out in order to synthesis a high dense and high aspect ratio of ZnO nanorods. It has been demonstrated that a high-density of ZnO nanorods with aspect ratio 15:1 can be successfully synthesized at an annealing temperature of 100^{o}C and 3 hours growth duration for via hydrothermal. Meanwhile for PECVD, a high aspect ratio of 12:1 ZnO nanorods successfully synthesized at 4nm gold (Au) catalyst with chamber pressure of 700mTorr. SEM and AFM analyses showed that the formation of ZnO nanorods via hydrothermal is significantly influenced by the seeds particle morphology while for PECVD, the Au nanoparticle size and the proper ratio of vapors components are the major parameter affecting the ZnO nanorods growth. The grown ZnO from both samples is of the wurtzite crystal type based on raman shift E_2(high) of 436cm^{-1}.An electrical characteristics via four point probles been conducted and the results showed that the resistivity of the ZnO grown via hydrothermal and PECVD are $4.47 \times 10^{-3}\Omega.cm$ and $47 \times 10^{-3}\Omega.cm$ respectively. The sensitivity to oxygen gas for both ZnO nanorods has been compared in ambient environment and the results indicated that the ZnO grown through the hydrothermal methods is more sensitive of the two in which a change of resistance of 57.67%. It has also been elucidated that the gas sensor sensitivity is also increased with decreasing ZnO nanorods dimension. The response time, selectivity, resolution, stability, temperature effect and humidity effect of the gas sensor have also been characterized. The sensor drift due to fluctuation of temperature, humidity and ageing time in real environment has successfully been compensated via baseline manipulation method and the results show the 99.5% accuracy compared to commercial sensor.

CHAPTER 1

INTRODUCTION

1.0 Research Motivation

The safe oxygen gas limit is important to be measured and monitored, particularly in confined space such as in submarine, space shuttle, airplane or any poor ventilation area likes quarry, tunnel, drainage pipe and oil-rig platform (IACS, 2007). According to OSHA (Occupational Safety and Health Act) standard as shown in Table 1.1, oxygen concentration lower than 19.5 % is deemed hazardous while an oxygen gas concentration level beyond 23.5 % is categorized as flammable. Northwest Occupational Health and Safety (NWOSH) detailed the acute effect to the human when experiencing the lack of oxygen concentration as shown in Table 1.2. As shown in Table 1.2, the deficient of oxygen gas concentration will seriously affect the physical and mind consciousness when the oxygen reaches to 16 % and risks to loss of life immediately when reaching 12 %. The danger of depletion oxygen has also been documented by European Industrial Gases Association (EIGA). Edward et al. (2007) reported that injury or death due to oxygen deficiency is a common hazard in many chemical, refinery and other industries. Toxic gas is often to blame when workers die unnecessarily due to asphyxiation in environments where the oxygen is actually depleted by gases such as nitrogen. In view of these, a sensitive and reliable oxygen gas sensor with the capability to detect the oxygen gas level within the safely limit as defined by the OSHA standard needs to be developed.

Table 1.1: Safe oxygen level in indoor environment based on OSHA standard

Oxygen Concentration (%)	Condition
>23.5	Flammable
20-23	Safe
<19.5	Hazardous

Table 1.2: Acute effect to human body due to exposure of deficient oxygen in atmosphere based on NWOHS standard

Acute Effect	Concentration (%)
Increased heart and breathing rate, some loss of coordination, increased breathing volume, impaired attention and thinking	16
Abnormal fatigue upon exertion, emotional upset, faulty coordination, impaired judgement	14
Very poor judgement and coordination, impaired respiration that may cause permanent heart damage, nausea and vomiting	12
Nausea, vomiting, lethargic movements, unconsciousness, inability to perform vigorous movement or loss of all movement followed by death	< 10
Convulsions, shortness of breath, cardiac standstill, death in minutes	< 6
Unconsciousness after one or two breaths	< 4

1.1 Nanostructured Metal Oxide Oxygen Gas Sensors

At present, there are many types of gas sensor technology such as polymer based, acoustic, chromatograph, calorimetric, optical, and metal oxide semiconductor. With the exception of metal oxide semiconductor, these gas sensor technologies are known to have suffered from problems such as short life span, limit to low temperature operation, expensive, and complexity in design which limit the wide range of applications. On the other hand, the metal oxide semiconductor technology is relatively inexpensive compared to other sensing technologies, able to miniaturize, robust in structure, stable at high temperature operation, lightweight, high material sensitivity and quick response times. In addition, high compatibility with semiconductor fabrication technologies has enabled the production of low cost sensor with improved sensitivity and reliability to be realized.

Nowadays, the nanotechnology is leading the development of highly sensitive metal oxide based gas sensor. Functionalization of the metal oxide at nanoscale level will provide a lot