THE EFFECT OF VARIOUS DOPANTS ON ZNO SURFACE FOR GAS SENSOR APPLICATION

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Specially dedicated

to my supervisor Dr. S. M. Sultan and my family who encouraged

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ABSTRACT

One-dimensional (1-D) nanomaterials have drawn a lot of attention in last few decades because of their novel and unique properties and a wide range of applications. ZnO nanomaterials are among the most important 1-D nanomaterials due to their semi-conductive, piezoelectric, and biocompatible properties. With these unique characteristics, ZnO became one of the most important nanomaterials in scientific research and applications nowadays. ZnO is a member of group (II-VI) semiconducting compounds and exhibits n-type character so it can be easily doped by substituting Zn with group III elements (Al, Ge, In) and O with group VII elements (Chlorine, Iodine). Dopant effect can modify the electrical properties of ZnO which is an advancement for gas sensor. The large surface area of the ZnO 1-D nanostructures makes them attractive for gas sensing, as it can absorb as much of the target gas as possible particularly at low concentrations. Consequently, the electrical conductivity of ZnO significantly affected by the adsorption and desorption of gas species on their surface. In this work, simulation of pure and doped ZnO nanosheet are performed and the dopants effect on ZnO electronics, electrical and sensing properties are observed by using Quantum Wise simulation by ATK-VNL. The gas sensor based ZnO nano-structure are fabricated by the atomic scale simulation using Quantum Wise software VNL-ATK and examined with group III (Al) and group VII (F) effect on ZnO towards gas sensor applications. Pure ZnO found to be sensitive towards group III and Group VII elements (Aluminum, Fluorine) by substituting a single O and a single Zn atom respectively from the bulk. It was observed an increased on the Fermi energy level when introducing the dopants on the ZnO nano surface. The calculated Fermi levels were -3.4464 eV, -3.075495eV and -3.1921eV respectively for pure, F-doped and Al-doped ZnO. The sensitivity performance towards CO gas revealed, F-doped ZnO exhibits a 67% sensitivity. This value is higher compared to pure and Al-doped ZnO which were 28% and 56% respectively. This shows F-doped ZnO nanosheet can enhance the sensitivity towards CO gas sensing.

ABSTRAK

Satu dimensi (1-D) nanobahan telah menjadi satu tarikan dalam beberapa dekad kebelakangan ini disebabkan oleh ciri-cirinya yang unik dan juga boleh diguna dalam pelbagai kegunaan. ZnO nanobahan adalah antara yang terpenting dalam kumpulan 1-D nanobahan disebabkan mempunyai ciri-ciri seperti separa berkonduksian, piezoelektrik dan bioserasi. Hari ini, dengan ciri-ciri unik tersebut ZnO telah menjadi salah satu nanobahan yang terpenting dalam kajian saintifik dan pelbagai kegunaan. ZnO ialah semikonduktor sebatian dari kumpulan (II-VI) dan menunjukan ciri jenis-n, oleh itu ianya menjadi lebih mudah untuk didopkan dengan menggantikan Zn atom kepada unsur-unsur kumpulan III (Al, Ge, In) manakala O atom dengan unsur-unsur kumpulan VII (Cl, I). Kesan dopan boleh mengubah sifat elektrik ZnO yang merupakan satu kemajuan untuk sensor gas. Luas permukaan yang besar bagi 1-D nanostruktur ZnO membuatkannnya menarik untuk mengesan gas seperti boleh menyerap sebanyak mungkin gas sasaran walaupun dalam kandungan yang sedikit. Hal ini demikian, kekonduksian elektrik ZnO secara jelas dipengaruhi jerapan dan penyeharapan spesies gas atas permukaanya. Dalam kajian ini, simulasi terhadap ZnO tulen dan ZnO nanokeping yang didopkan telah dibuat termasuklah menganalisa pengaruh kesan dopan terhadap sifat elektronik dan penderiaan ZnO menggunakan Quantum Wise (ATK-VNL). Bagi sensor gas ZnO nanostruktur yang telah difabrikasikan melalui simulasi berskala atom dan juga pemeriksaan kesan dopan Al dan F dalam ZnO terhadap penggunaan sensor gas telah menggunakan perisian Quantum Wise iaitu ATK-VNL. ZnO tulen didapati lebih peka apabila menggantikan O atom dengan Al dan Zn atom dengan F. Ianya telah dikesan meningkatkan tenaga aras Fermi apabila nanostruktur ZnO didopkan. Aras Fermi yang telah dikira bagi ZnO tulen, F-dop ZnO dan Al-dop ZnO masing-masing adalah -3.4464 eV, -3.075495eV dan -3.1921eV. Prestasi penderiaan terhadap gas CO juga memperlihatkan bahawa F-dop ZnO menunjukkan peratus kepekaaan sebanyak 67%. Nilai ini adalah lebih tinggi dibandingkan dengan ZnO tulen dan Al-dop ZnO yang masing-masing memiliki peratus kepekaan sebanyak 28% dan 56%. Ini menunjukkan F-dop ZnO nanokeping boleh meningkatkan kepekaan penderiaan terhadap gas CO.

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LIST OF ABBREVIATIONS

ZnO	-	Zinc Oxide
Al-ZnO	-	Aluminum Doped Zinc Oxide
F-ZnO	-	Fluorine Doped Zinc Oxide
CO	-	Carbon Monoxide
DFT	-	Density Functional Theory
NEGF	-	Non-Equilibrium Green’s Function
LDA	-	Local Density Approximation
LCAO	-	Linear Combination Of Atomic Orbitals
GGA	-	Generalized Gradient Approximation
PBE	-	Perdew--Burke—Ernzerhof
KS	-	Kohn-Sham
TS	-	Transmission Spectrum
DOS	-	Density Of State
ATK	-	Atomistix ToolKit
VNL	-	Virtual Nano-Lab

LIST OF SYMBOLS

E	-	Energy
$n_L(E)$	-	Carrier Source
$n_R(E)$	-	Carrier Sink
$T(E)$	-	Transmission Coefficient
E_g	-	Energy Band Gap
E_f	-	Fermi Level
T	-	Temperature
e^-	-	Electron
S	-	Sensitivity
I-V	-	Current Voltage

CHAPTER 1

INTRODUCTION

1.1 Background Study

The earliest electronic application of ZnO was the radio set year 1920's by creating a Schottky barrier with wiring a ZnO crystal with a copper wire, which provided the amendment needed for converting the AC radio waves to DC signals [1]. ZnO was widely spread in electronics for the use of varistors allowing reliable surge protection. As material science started progressing during 20th century, ZnO got more appreciation in the material investigation. The role of semiconductor nanostructure has the colossal impact on the expansion of nanotechnology in last eras such as functional devices including Gas Sensor [2] And Biological Sensor [3], Field Effect Transistors [4], Light Emitting Diodes [5], solar Cells [6] And Nano-Generators [7]. Among many semiconducting oxides for instance SnO_2, NiO, MgO, CdO, ZnO have captured the most attentions for nano-device applications due to its hexagonal wurtzite structure type, electronic distribution, and polarity [8].

In 1954 ZnO was confirmed as an n-type material characteristically [9] and the light emission from ZnO was also drawing attention among researchers in Germany [10].

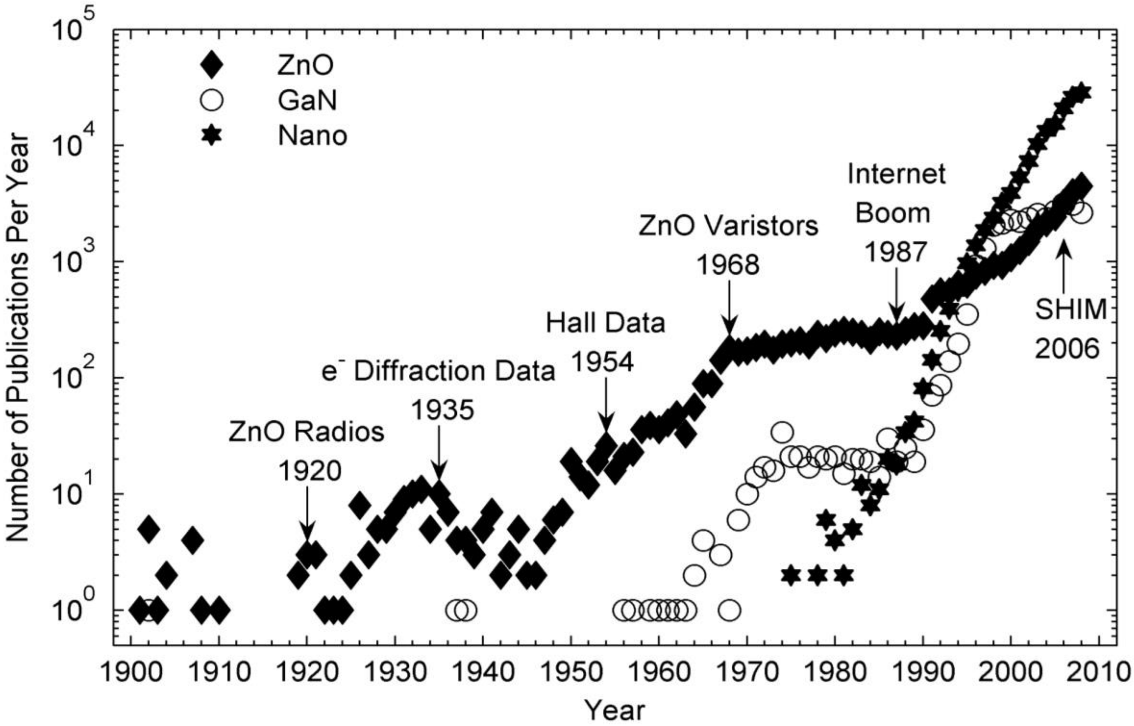

Figure 1.1: Investigation into the Properties of ZnO [11]

ZnO has proved to be a propitious semiconductor material for numerous applications. Many researches have been carried out and published over the decades on ZnO and ZnO related materials. The Figure 1.1 above shows the steady growth of investigations on ZnO in every ten years.

ZnO possesses direct and extensive band gap of 3.37 eV with a large free-exciton binding energy [12-16] at room temperature. The optical and piezoelectric properties of ZnO make it a noble application for transducers, sensors, and energy generators, as well as in photo-catalysis for hydrogen production [17]. Although, the vast use of ZnO in many applications was proceeding, ZnO was slowed down in electronics devices due to the absence of control over its electrical conductivity as ZnO crystal found naturally n-type which made it more debatable and cause of advance research [18–20]. To control the unpremeditated n-type conductivity and to attain p-type conductivity in ZnO many research started focusing on its semiconductor properties. Optical, magnetic and electrical properties of a semiconductor can be overelaborated by impurities or doping with other elements. Different group elements as dopants have various effect on semiconductor materials for numerous applications.

Doping of ZnO with group I-VII elements Li, Na, K [21], Mg [22], Ga [23], Si [24], N [25], S [26], Cl [27], transitional elements such as Cr, Fe, and Ni [28] and rare earth elements La [29] have been confirmed and reported to bring additional enhancements on optical, structural, electrical, and magnetic properties of ZnO. P-type conductivity on ZnO is still controversial as the properties of these acceptor-doped samples are often unsteady [30-34].

Both pure and doped ZnO nanostructure have verified their capability in many applications among the earliest learnt metal oxide materials [35]. The furthermost common application of semiconducting metal oxide (SMO) is the resistive element in gas sensor between different applications. ZnO is the 2nd most oppressed solid for gas detecting after SnO_2 because of its distinctive structure and possessions [36].

The environment is critically getting polluted by the growing energy consumptions in today's world, which is affecting human and animal safety in terms of their health. Hazardous gases are created from the burnt energy such as painting, smoking, petrol filling, building, diggings of polluted soils, landfill procedures, entering restricted spaces, etc. Many investigations have brought out to detect those toxic gases such as CO [37], O_2 [38], LPG [39], NO_2 [40], H_2S [41], Alcohol [42] and to protect the environment from their harmful affect all over the world. An efficient study led the knowledge proceeding the deviations in the electrical properties of semiconductor materials due to the iteration of gas molecules at the surface and that study driven the research on metal oxides for gas sensing application further [43-45]. Japan invented and published a research paper on gas sensor utilized by semiconductor catalyst mechanism, which indicated the measurement of resistance change in a metallic oxide (ZnO) when it comes in contact with a gas in 1962 [46]. In addition, further investigation discovered metal impurities or doping can enhance the reaction of the gas sensor towards an object gas by reducing particle size, by altering operation temperature and humidity. The selection of metal oxide with respect to the types of gas and effects of dopants on the semiconductor material were also studied to have a strong understanding about the connection between the metal oxide and gas. Constant advancement of nanoscience and technology has brighten the field more and steered the sensor technology to drastic revolution [47-63].

In this current study, the effect of various dopants on ZnO surface such as electrical properties and the gas sensitivity of pure and doped ZnO toward targeted gas have been focused on by using Quantum-wise Atomix Toolkit for simulation process. Initially Aluminum (Al) and fluorine (F) as dopants and toxic gas Carbon Monoxide (CO) have been chosen for the research.

1.2 Problem Statement

The wide band gap and crystal structure of ZnO made it the most potential candidate for gas sensing among other metal oxides. Numerous studies have been done on gas sensing properties of ZnO over decades by using synthesis methods for example Chemical Vapor Method (CVD), Thermal Evaporation, Laser Ablation, Solution Methods and ARC Plasma Reaction etc. Most synthesis methods used are time consuming and costly for the whole process. So, the simulation using Quantum Wise is a better way to examine and predict the sensitivity and the properties of both pure and doped ZnO.

1.3 Objectives of Project

The main purpose of the study is to design a ZnO nanosheet and observe the dopants effect on ZnO electronics and electrical properties and compare gas sensing properties on the both pure and doped models by using Quantum Wise simulation by ATK-VNL.

To characterize the electrical properties of pure ZnO nanosheet in Quantum wise Simulation tool.

1. To compare the band structures and electrical properties with effect of dopants (Al and F) on ZnO nano-sheet.

2. To analyze and compare the sensing properties of pure and doped ZnO nanostructure under the influence of dangerous gas (CO).

1.4 Scope of Study

These are the scopes of study:

1. Simulation of both conventional wurtzite nanosheet pure and doped ZnO using Quantum Wise ATK VNL software package.

2. The dopant elements Aluminum (group III) and Fluorine (group VII) will be used to analyze the electrical and sensing performance.

3. Measure the sensing performance based on one molecule of CO gas. Verify the gas sensing parameters such as gas sensitivity (S) and limit of detection for ZnO-based gas sensor with the use of CO gas.

1.5 Research Outline

The framework of this thesis is divided into five chapters. The first chapter has discussed the introduction of the project. These include project background, problem statements, research objectives, scope of project work, the organization of thesis and planning for the project work for both semester.

The next Chapter discusses the literature review related to this research project. Literature review is established on the previous research work done by the researchers, including the published thesis and journal. Initially the main focus of this literature analyses was to recognize the basic electrical and electronic properties and the doping effect on ZnO achieved by several experiments performed. Later on the studies fixated on the gas sensitivity of pure and doped ZnO. Many conclusive results and descriptions of ZnO properties can be figured out from all these resources, which were really beneficial for this current study.

Chapter three demonstrates the methodology of this research project. The steps of the project are summarized in flowcharts and figures in this part.

Chapter four designates the main results of this project, where the electronic and electrical properties of pure and doped ZnO obtained from the simulation by ATK VNL have been presented. Moreover the proposed result of the project which was to find the sensitivity of pure and doped ZnO towards the gas CO are exposed.

The conclusion part of the project is enclosed in Chapter five. All the results and discussions made in Chapter four were concluded with the proposals for future work, which can be done on ZnO by simulation process.

1.6 Summary

Due to the rich basic properties of ZnO, it can be doped by different group member on the periodic table to tune its band gap and thus can be very useful candidate for several nano-electronic devices. These dopants effect and sensitivity can be easily and effectively simulated on ATK VNL before going into actual physical configuration of the device. In this way researchers can save cost and time and avoid trial and error process of experimental studies.

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