EFFECT OF ANNEALING TEMPERATURE ON STRUCTURAL PROPERTIES OF ALUMINIUM DOPED ZINC OXIDE NANOPARTICLES SYNTHESIZED VIA SOL GEL AUTO COMBUSTION

This report is submitted in accordance with requirement of the University Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering

by

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Tajuk: **EFFECT OF ANNEALING TEMPERATURE ON STRUCTURAL PROPERTIES OF ALUMINIUM DOPED ZINC OXIDE NANOPARTICLES SYNTHESIZED VIA SOL GEL AUTO COMBUSTION**

Sesi Pengajian: **2017/2018 Semester 2**

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Date : …………………………

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Hons). The member of the supervisory committee are as follow:

……………………..................................

(Dr. Mohd Shahadan bin Mohd Suan)

(Project Supervisor)

ABSTRAK

Kajian ini dijalankan adalah untuk mengkaji kesan suhu penyepuhlindapan pada sifat-sifat struktur dan optik aluminium terdop nanopartikel zink oksida yang disintesis melalui kaedah pembakaran auto sol gel. Zink oksida dengan sifat unik seperti jurang band yang lebar iaitu 3.37 eV dan tenaga exciton yang besar ~ 60 meV, mempunyai banyak aplikasi terutama sebagai bahan semikonduktor. Penambahan aluminium ke dalam zink oksida meningkatkan sifat zink oksida itu sendiri termasuk meningkatkan sifat ketahanan elektrik. Telah dilaporkan bahawa suhu penyepuhlindapan yang berbeza mempengaruhi sifat-sifat aluminium terdop zink oksida. Kaedah sintesis yang digunakan mempunyai komposisi komposisi kawalan yang lebih baik dan kurang benda asing berbanding dengan kaedah konvensional. Butiran proses dan mekanisme yang digunakan untuk sintesis nanopartikel melalui kaedah kos mudah dan rendah, sol gel pembakaran automatik untuk mendapatkan ketulenan tinggi aluminium zink oksida dijelaskan. Suhu yang dipilih yang diubah dalam proses penyambungan ialah 400 ° C, 500 ° C, 600 ° C, 700 ° C, dan 800 ° C. Nanopartikel yang disediakan akan diuji kepada pelbagai teknik kecirian. Sifat-sifat struktur akan dicirikan dengan menggunakan mikroskop pengimbasan pelepasan elektron (FESEM) dan pembelauan sinar-x (XRD). Sementara itu untuk sifat optik, spektroskop transformasi inframerah fourier (FTIR) dan spektroskop ultraviolet visible (UV-Vis) digunakan.

ABSTRACT

The aim of this study is to investigate the effects of annealing temperature on the structural and optical properties of aluminium doped zinc oxide nanoparticles synthesized via sol gel auto combustion method. Zinc oxide with unique properties such as wide band gap, 3.37 eV and large exciton energy of ~ 60 meV, has many applications especially as semiconductor materials. The doping of aluminium to zinc oxide improves the properties of zinc oxide itself included increase the electrical toughness property. It has been reported that dissimilar annealing temperature affects the properties of aluminium doped zinc oxide compound. The method used has better control compound of composition and less impurities compared to conventional methods. The details of process and mechanism responsible for the synthesis of nanoparticles by simple and low cost method, sol gel auto combustion to get high purity of aluminium doped zinc oxide are explained. The chosen temperatures that altered in calcination process are 400°C, 500°C, 600°C, 700°C, and 800°C. The prepared nanomaterials are subjected to various characterizations. The structural properties will be characterized by using field emission scanning electron microscope (FESEM) and x-ray diffraction (XRD). Meanwhile for optical properties, fourier transform infrared spectroscope (FTIR) and ultraviolet visible spectroscope (UV-Vis) are used.

DEDICATION

TO MY BELOVED PARENT,

Mohamad Yusof Bin Kasnan with Napsiah Binti Hassan

For their supports in my whole life

TO MY HONOURED SUPERVISOR,

Dr. Mohd Shahadan Bin Mohd Suan

For his advices, support, motivation, and patience during completion of this project

TO ALL STAFFS & TECHNICIANS,

For their cooperation and advices to complete this project

AND TO ALL MY COLLEAGUE,

For their encouragement, cooperation and effort in this study

Only Allah S.W.T can repay your kindness and hopes Allah S.W.T blesses our lives

ACKNOWLEDGEMENT

In the name of Allah, the Most Gracious and Merciful God, I would like to express my grateful as I managed to complete my undergraduate project for Bachelor Degree of Manufacturing Engineering within the time given. All thanks to Allah as only He can give permission for me to complete this project.

My deep hearted appreciation goes to my supervisor Dr. Mohd Shahadan Bin Mohd Suan for all his guidance, ideas, thoughts and encouragement throughout the course of this study. Grateful appreciation to all Universiti Teknikal Malaysia Melaka staffs especially in Faculty of Manufacturing Engineering for their cooperation with me throughout this period of time.

And finally, my deepest hearted appreciation goes to my family, especially my parent, Mohamad Yusof Bin Kasnan and Napsiah Binti Hassan for their prayer and loving support in my whole life, without them I may not manage to finish this project on time. Thanks to all my colleagues that may involve whether directly or indirectly during the completion of this project.

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Al	-	Aluminium
$Al(NO_3)_3$	-	Aluminium Nitrate
AZO	-	Aluminium Doped Zinc Oxide
B	-	Boron
$C_6H_8O_7$	-	Citric Acid
$CdSnO_3$	-	Cadmium Stannate
eV	-	Electron Volt
DTA	-	Differential Thermal Analysis
FESEM	-	Field Emission Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared Spectrometer
Ga	-	Gallium
In	-	Indium
IR	-	Infrared
JCPDS	-	Joint Committee on Powder Diffraction Standards
LED	-	Light Emitting Diodes
NH_4OH	-	Ammonia Hydroxide
O	-	Oxygen
Pb	-	Lead
Pt	-	Platinum
Ru	-	Ruthenium
TCO	-	Transparent Conductive Oxide
TEM	-	Transmission Electron Microscope
TGA	-	Thermo Gravimetric Analysis
UV-Vis	-	Ultraviolet-visible Spectroscope
VCS	-	Volume Combustion Synthesis
Zn	-	Zinc
$Zn(NO_3)_2$	-	Zinc Nitrate
ZnO	-	Zinc Oxide

CHAPTER 1

INTRODUCTION

1.1 Background Study

Zinc oxide is an inorganic composite with the formula of ZnO. ZnO is extensively used as an additive in various materials and products (Sabir, 2014). Zinc oxide is a direct, wide band gap semiconductor material with many desired properties for optoelectronics, transparent electronics, spintronic devices and sensor applications. ZnO has been commonly used in its polycrystalline form for over hundred years in a wide range of applications. ZnO has numerous attractive characteristics for electronics and optoelectronics devices. It has direct bandgap energy of 3.37eV which makes it transparent in visible of light and operates in the UV to blue wavelengths. The exciton binding energy is ~60meV which improve the luminescence efficiency of light emission. The room temperature electron Hall mobility in single crystal ZnO is ~200cm² V^{-1} and has high saturation velocity (Jagadish et al., 2006).

Epitaxial layers and single crystal will be important for the development of optoelectronic (blue and ultraviolet light emitters and detectors), piezoelectric and spintronic devices. Epitaxial ZnO also acts as a semi-conducting transparent thin film which is important for solar cells, gas sensors and wavelength selective applications. (Jagadish *et al.*, 2006). Doping is a practical method to intensify optoelectronic properties of ZnO. The small amount of doping element alters the structural and morphological properties of ZnO as well. Element of the group III in periodic table such as Al is desired element as doping element because their ionic radii are close to radii of Zn^{2+}. Al also is applicable in transparent conducting oxide due to low resistivity of AZO (R. Ebrahimifard *et al.*, 2014).

Nanoparticles are wide class of materials that include particulate substances, which has one dimension less than 100 nm at least (Laurent et al., 2010). Nanoscaled particles of semiconductor materials have attained great achievement in recent years due to their desirable properties and applications in different field especially electronic industries. Recently many researches and experiments have proved and improved the efficiency of ZnO materials by producing nanostructures where each nano dimension is reduced to compose nanowires, thin films and other structures for plenty of applications. Zinc oxide nanoparticles have a great benefit to be applied in a catalytic reaction process due to high catalytic activity and vast surface area. It has been used for its catalytic, electrical, optoelectronic and photochemical properties.

The history of nanoparticles began in the century of Mesopotamia, where it was used to produce glittering effect on the pot surface. Polycrystalline ZnO was used for the purpose of medical and pharmaceutical industries and medical technology in early 1990's. Gold nanoparticles was first developed by Turkevich and then improved by Frens by using electrochemistry technique. Nowadays, the ZnO nano-structure has been widely expand and increasing by years.

The synthesis method for ZnO is crucial to develop the nanoparticles. There are many methods which are commonly used to synthesize material of ZnO such as chemical deposition, sol gel method, auto combustion method, solid state reaction, precipitation method, hydrothermal and solvothermal method.

1.2 Problem Statement

In the past ten years, the research on zinc oxide (ZnO) as a semiconductor material has been revived and rapidly expands. The high electron mobility, high thermal conductivity, wide and direct band gap and large exciton binding energy make ZnO suitable for a varied range of devices, including transparent thin-film transistors, light-emitting diodes and laser diodes that operate in blue and ultraviolet area of the spectrum. In spite of the recent rapid developments, controlling structural and optical stabilities of ZnO has remained a major challenge.

It has been stated that the properties of ZnO has increased, include wider band gap of 3.37 eV, greater conductivity and improve thermal stability after doped with group III elements. Hence, among these elements, Al is chosen to be doped into ZnO due to its availability, non-toxicity, simple doping process and can be obtained with low cost. Nevertheless, the most important advantage is the doping of Al can increase the electrical toughness of ZnO.

The properties of ZnO are also determined by its form where the nanoparticles ZnO showed higher performance compare to the bulk ZnO. A nanoparticle is a form of structure with sizes the nm range. Particles which bonded together or individual with size less than 100nm can be considered as nanoparticles. In the form of nanoparticles, ZnO is reported to have higher reactivity due to large surface area hence resulted with enhanced electrical and optical properties. There are several methods used for synthesis of nanoparticles such as solid reaction, sol-gel method, precipitation method, hydrothermal method and auto combustion.

The sol-gel auto combustion reaction attracted much attention in synthesizing highly pure nanoparticles due to its simple process and better control of compound compositions. The combustion process occurred at high temperature can vaporized all impurities while the annealing process afterward provide thermal and structural stability to the powder. Different annealing temperatures can affects the properties of compound whether in structural, electrical or optical. Thus, in this study, the optical and structural properties of ZnO doped with Al synthesized via sol-gel auto combustion will be investigated in effects of the annealing temperatures

1.3 Objectives

1. To synthesize Al doped ZnO nanoparticles using sol-gel auto combustion reaction annealed at different temperature.
2. To characterize and investigate the effects of annealing temperature on the structural properties of annealed Al doped ZnO.

1.4 Research Scope

This research work scope is synthesizing and characterizing Al doped ZnO nanoparticles via sol-gel auto combustion method with specified annealing temperatures which are 400°C, 500°C, 600°C, 700°C and 800°C. The annealing temperature is the key parameter to improve the electrical conductivity in the ZnO. The raw materials were zinc nitrate solution, aluminium nitrate solution, citric acid, and ammonia solution. The processes involved during synthesis of Al doped ZnO are mixing, heated solution, auto combustion, and calcination. Structural properties such as type of elements, crystalline size, microstructure, and morphology of ZnO nanoparticles were characterized by using X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) to investigate the outcomes of each parameter. A scanning electron microscope is used to obtain the high resolution image with magnification of 50,000 times. The optical absorption and specifications for characterization were set within the range value of 1000 to 1200 cm-1 for spectral and 0.3cm-1 for resolution Fourier Transform Infrared Spectroscope (FTIR).

1.5 Significant of Research

The project significances are as follows:

a) To study the structural properties of Al doped ZnO nanoparticles synthesized via sol gel auto combustion.

b) To develop more information and also further understanding about the role of ZnO nanoparticles when it doped to the Al to improve the properties of the ZnO.

c) To develop an alternative semiconductor material that gained from simple synthesis method.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, the basic properties of zinc oxide will be explained in details in the section 2.2. The forms of ZnO are explained in section 2.3. After that, the microstructure and optical properties of ZnO nanoparticles are discussed in section 2.4.1 and 2.4.2 respectively. Moreover, doping of zinc oxide with various elements to improve electrical conductivity will be discussed in section 2.5. Next, the chosen dopant element which is aluminium to be doped with ZnO nanoparticles will be explained in section 2.6. In section 2.7, the applications of ZnO will be briefly explained due to its abilities in various industries. The synthesis of ZnO in various methods such as sol gel method, hydrothermal method and the others will be discussed. The chosen method in this study which is sol gel auto-combustion will be discussed in details in the section 2.8.4. Lastly, characterization of Al doped ZnO nanoparticles by using various type of machines such as X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), thermo gravimetric analysis (TGA) and differential thermal analysis (DTA), ultraviolet visible spectroscopy (UV-Vis) also will be discussed in this chapter.

2.2 Zinc Oxide

Zinc oxide has unique physical and chemical properties. Its high chemical stability, broad range of radiation absorption, high electrochemical coupling coefficient, and high photostability made it as a multifunctional material (Kolodziejczak-Radzimska &

Jesionowski, 2014). ZnO as an II-VI transparent oxide compound is a wide band gap semiconductor with a direct band gap energy of 3.37 eV and exciton binding energy of 60 meV at ambient environment. Naturally, oxygen vacancies make ZnO as an n-type semiconductor, while introducing new elements such as nitrogen would be able to make it p-type. These properties allow ZnO to be used in LEDs, dye sensitised solar cells, transparent conducting oxide and sensors (Ebrahimifard et al, 2012).

ZnO can appear in three types of dimensional which are one-dimensional (1D), two-dimensional (2D), and three-imensional (3D) structure. The examples of 1D structures is nanorods, springs, helixes, needles, ribbons, rings, wires, tubes, belts and combs. Meanwhile, the examples of 2D structure are nanoplate or nanosheet and nanopellets. 3D structures give examples such as flower, snowflakes, dandelion, and coniferous urchin-like (Jesionowski, 2014).

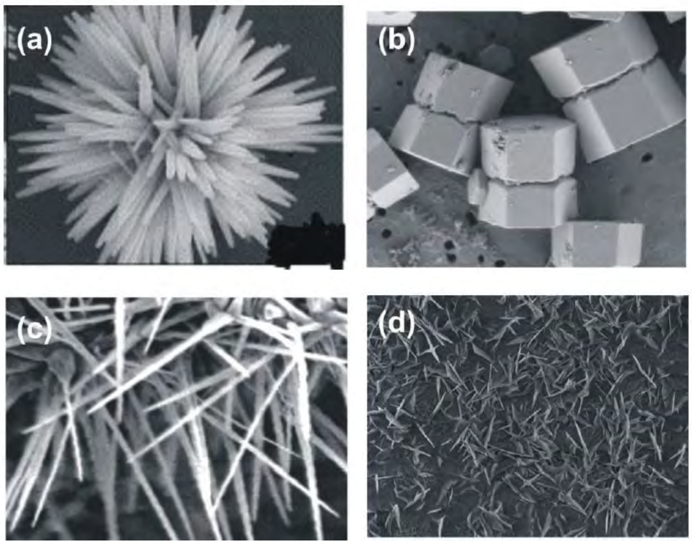

Figure 2.1 The examples of zinc oxide structure (a)flower (b)rods (c)(d) wires

Table 2.1 Basic properties of zinc oxide

Basic ZnO Properties		
1.	Appearance	White Solid
2.	Odor	Odorless
3.	Molecular Weight	81.38 g/mol
4.	Crystal Structure	Wurtzite
5.	Coordination Geometry	Tetrahedral
6.	Lattice Constant	a = 3.25 Å, c = 5.2 Å
7.	Band Gap	3.3 eV
8.	Solubility in Water	0.0004% (17.8°C)
9.	Refractive Index (μ_D)	2.0041
10.	Density	5.606 g/cm^3
11.	Melting Point	1975°C
12.	Flash Point	1436 °C

Table 1 shows the other basic properties of ZnO that made the material very unique and multifunctional (Uikey & Vishwakarma, 2016).

2.3 Zinc Oxide Forms

Zinc oxide can appear in three different types of form which are thin film, powder and nanoparticles. Transparent conductive oxide (TCO) thin film such as ZnO thin film is most important basic components in producing photoelectric devices such as flat-panel display and solar cells. TCO films with nearly metallic conductivity and high transmission of visible light has been extensively studied in recent years (Wang et al., 2017). ZnO nanopowder is widely used in electronic components such as varistor (Jesionowski, 2014).

2.4 Zinc Oxide Nanoparticles

The characteristics of nanoparticles are contrast from that bulk material. Generally, ZnO nanoparticles illustrate two types of emissions which are in ultraviolet UV domain state centered at approximately 380nm and another in visible region in the range of 450-765 nm. Commonly, ZnO crystallizes in two main forms which are hexagonal wurtzite and cubic zinc blende. Figure 2 and Figure 3 show both of the structures. The most stable at environmental conditions is the hexagonal wurtzite. Cubic zinc blende is not stable but it can be stabilized. It can be stabilized by mounting ZnO on substrates with cubic lattice structure. For both structures, the zinc and oxide centers are known as tetrahedral (Uikey & Vishwakarma, 2016).

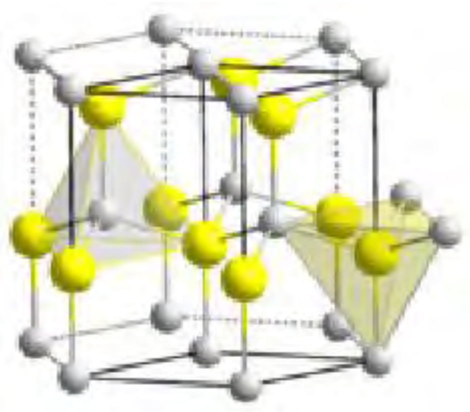

Figure 2.1 Hexagonal wurtzite of ZnO

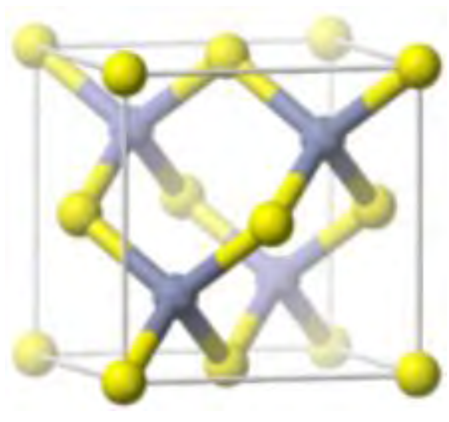

Figure 2.2 Cubic zinc blende of ZnO