UNIVERSITI TEKNOLOGI MARA

STUDY ON NANOSTRUCTURED ZINC OXIDE THIN FILMS CHARACTERISTICS

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Thesis submitted in fulfillment
of the requirements for the degree of
Master of Science

Faculty of Mechanical Engineering

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AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the results of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

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ABSTRACT

The Nanostructured zinc oxide (ZnO) materials in thin film have been achieved using electrochemical deposition (ECD) method. The morphology, crystal structure and optical properties of ZnO nanostructures have been characterized. The best potentials for deposition were -1.0V and -1.1V using ECD method. Analysis using (FESEM) showed that ZnO nanoparticles and nanorods growths uniformly. The XRD patterns of ZnO nanostructures thin films shows evident in good arrangement of crystal structure properties that has been investigated in high deposited temperature at 95°C and annealed at 500°C. It is proved that ZnO thin film texture surface with the c-axis perpendicular to the substrate surface. Deposition of ZnO seed catalysis growth of hexagonal wurtzite structure of ZnO and exhibited good arrangement of ZnO nanorods growth investigated at -1.0V, -1.1V, -1.2V, 1.3V and -1.4V of the potential applied. The highest transmittance spectra of -1.0V potential applied showed 80% transmittance spectra compared to that of other potentials which deposited at high deposition temperature. For piezoelectric properties, results at -1.0 V, -1.1 V and -1.2 V of ZnO thin films can give signal corresponding to the average of current output 600 μA, 200 μA and 50 μA, respectively. As a conclusion, the excellent ZnO nanostructures properties growth by ECD method has been achieved for the best deposition potential at -1.0 V and -1.1 V. Otherwise to improve the crystallites of ZnO has been prepared at high temperature deposition 95°C compare low temperature deposition. The high percentage transmittance has been exhibited at 80% after annealed in oxygen furnace to improve the optical properties.

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LIST OF ABBREVIATIONS

Abbreviations	
ZnO	Zinc Oxide
ZNRs	Zinc Oxide Nanoarrays
ZnO NW	Zinc Oxide Nanowires
MEMS	Micro-Electro-Mechanical System
FCC	Face-Centered Cubic
AFM	Atomic Force Microscopy
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscopy
FESEM	Field Emission Scanning Electron Microscopy
EDAX	Energy Dispersive Analysis X-ray Spectroscopy
XRD	X-ray Diffraction
PL	Photoluminensce
RS	Raman Scattering
PVD	Physical Vapour Deposition
CV	Cyclic Voltameter
ITO	Indium Tin Oxide
Mn	Manganese
Si	Silicone
SiC	Silicon Carbide
GaAs	Gallium Arsenide
GaN	Gallium Nitrate
NaCl	Rocksalt
ZnCl	Zinc chloride
$Zn(NO_3)_2$	Zinc nitrate
ECD	Electrochemical Deposition
PVDF	Polyvinylidene Fluoride
HMT	Hexamethylenetetramine
KCl	Potassium Chloride
DI Water	Deionised Water

ACG	Aqueous Chemical Growth
HT	Hydrothermal Treatment
CTA	Conversional Thermal Annealing
DSCs	Dye Sensitized Solar Cells
LED	Light Emitting Diode
PZT	Lead Zirconate Titanate
RF	Radio Frequency
FWHM	Full Width Half Maximum
Ref.	References
WE	Working Electrode
CE	Counter Electrode
Ag/AgCl	Silver/Silver Chloride

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CHAPTER ONE
INTRODUCTION

1.1 NANOTECHNOLOGY

The word "nano" indicates one billionth of a unit quantity, and research in nanotechnology has rapidly grown every year presenting good improvement in the use of nanomaterials. Nanotechnology refers to control and manipulation of materials in nanometer dimensions [1]. Nanomaterials is defined as material which has dimension or size up to 100 nm of the control of matter within the nanometer range, which has created novel and used to fabricate nanoscale devices. Synthesis of size and shape controlled nanostructures such as rods, cubes, wires, fibers, their self-assembly, properties and possible applications are under rigorous research. The importance of nanotechnology, state of the art technology centers with excellent processing, characterization and device fabrication facilities are being developed. Physical characteristics which are significantly different for these nanostructured materials have been attributed to their structural characteristics between isolated atoms and bulk macroscopic materials. "Quantum confinement" is basically due to changes in the atomic structure as a result of direct influence of the ultra-small length scale of the energy band structure. The electronic, mechanical, optical and magnetic properties of the nanoscale materials can all be attributed to the changes in total energy and structure of the system. In a free electron model, the energy of the electron and the spacing between energy levels, both vary as a function of $1/L^2$, with L as the dimension in that direction.

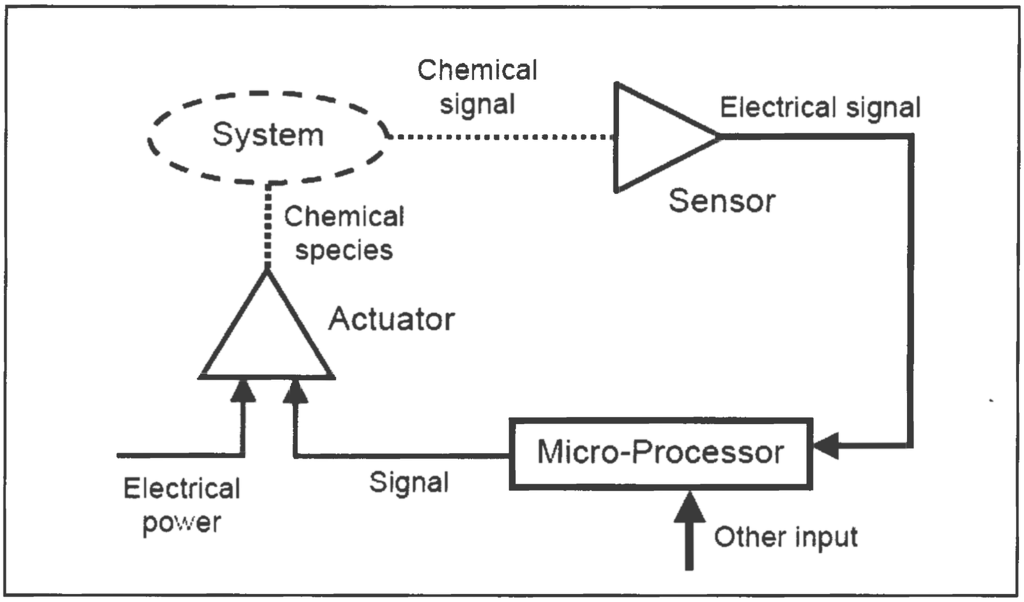
At nanoscale dimensions, the normal collective electronic properties of the solid become severely distorted and the electrons at this length scale tend to follow the "particle in a box" model, which might often require higher order calculations to account for band structure. The states of electron are more likely those found in the localized molecular bonds than the macroscopic solids. The main implication of such confinement changes in the system total energy, and also the overall thermodynamics stability. The chemical reactivity, being a function of the system structure and the occupation of the outermost energy levels, will be significantly affected at such length, causing a corresponding change in physical properties [2].

Most industrial and commercial activities involve control and monitoring environment with application such as safety, environmental and chemical plant instrumentation. Large impact in order to achieve the process or environmental control usually has the connection between the system and the environment to monitor the call sensor. Figure 1.1 shows the standard operation of feedback control system, in which the sensor and actuator have translated the other forms of energy (in this example, chemical) into and form electrical energy to the language of the microprocessors. This operation depends on the availability of appropriate input and output transducers commonly designated as sensor and actuators. Sensor and actuators are working in concert with the 'brain' of the system, the microprocessor. While microprocessor and the requiste analog to digital converters have been available for some decades, sensor and actuator technology has continued to lag, particularly with regard to achieving adequate sensitivity, reproducibility, and stability at reasonable cost [3]. Furthermore, MEMS has given a rapid progress over the past decade, in depositing high quality and reproducible oxide films onto silicon substrates for example high superconductors, high dielectric constant omit dielectrics and ferroelectrics.

In thin film technology, the development of semiconductor materials as sensor tools depends largely to the force-surface interaction which requires fast response time, improves selectivity through the use of arrays and reduces costs. An introduction of new technology known as "smart sensor" which uses small size of semiconductor sensors fabricated on silicon, (Si) substrate allows for integration with Si-based microelectronic circuits and micro-electro-mechanical system (MEMS), applied on-chip electronics for data acquisition and signal processing [4,5]

FIGURE 1.1

Schematic of Feedback Control System with Sensors and Actuators Capable of Translating other Forms of Energy (In this example, Chemical) Into and from Electrical Energy, to the Language of the Microprocessor [3]



In fact, in this research, the ZnO materials have been studied as sensor materials that attract many researchers, engineers and academician as it has served various applications such as material science and sensor fabrication field. Therefore, a number of industries and researchers are looking forward and have opened possible ways for them to grab the opportunity to supply the source of materials.

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1.2 PROBLEM STATEMENT

Most researchers have made some thought on how to develop and optimize the ZnO materials in the electronic device applications. This is due to the limitation of current materials such as silicon (Si) and gallium arsenide (GaAs) in the electronic device application at high temperature conditions, high operating speed and smaller scales are the most important parameters in electronic device fabrication. The ZnO materials have interesting characteristics which enable excellent in physical and chemical properties to improve the stability and durability.

In terms of application of ZnO nanostructures, despite their crystalline morphology, the orientation and surface structure must be well controlled during preparation process, and also can improve the quality of their optical and electronic properties. Unfortunately, ZnO nanostructures such as nanorods that were grown at relatively low temperature usually showed poor crystallization and optical properties too. Therefore, one of the significant differences between ZnO nanostructures and an epitaxial is larger surface area of the former. This is an advantage for some applications, for example sensor device, optoelectronic devices such as light emitting diode (LED) and solar-cell devices. So far, the knowledge about surface recombination or other surface effects in ZnO nanostructures is still limited, which is necessary for further investigation.

There are also cost reduction issue in electronic device fabrication. Therefore, the wide band gap semiconductor such as silicon carbide (SiC), gallium nitrate (GaN) and diamond materials are expensive to prepare and require higher cost to install appropriate equipment for the process. By introducing the metal oxide semiconductor such as ZnO has definitely revealed new performance in fabrication devices, and also cheaper process. ZnO can be fabricated as it is an abundant material, as well as easier to prepare and could be grown on non-crystalline substrate such as glass and polymers.

1.3 OBJECTIVE OF THE RESEARCH

Many researchers have proved that ZnO materials have excellent physical and chemical properties and have been selected as the best material to be fabricated in electronic devices. Hence, this research has been done with three main goals that focus on the following topics which are:

a. To synthesis the ZnO nanostructured thin film using the electrochemical deposition method
b. To characterize the ZnO nanostructured thin film using the electrochemical deposition method
c. To examine the ZnO nanostructured thin film at low and high deposition temperature bath

1.4 RESEARCH SCOPE

In this research, glass and indium tin oxide (ITO) substrates were coated with glass to observe the growth of ZnO nanostructured materials. Glass substrate has good properties such as stable in high temperature, electrical conductor and optically transparent. The glass substrate and ITO-coated glass has dimension of 20 mm x 20 mm x 1mm.

The electrochemical deposition (ECD) method has been used to grow the ZnO thin film by which the preparation of samples is simple, fast and economical as compared to current ZnO preparation method such as sputtering, chemical vapor deposition (CVD) and sol-gel method. The advantages of ECD method become very attractive for commercialization, especially in terms of cost effectiveness.

The sample preparation process was carried out in the laboratory in order to avoid any danger and to ensure a clean environment during experiment. The preparation steps need to be achieved as the ZnO materials can be found in various shapes such as particles, rods and wires in which strongly depend on the experimental parameters used. The types of precursors used, different potential applied, different deposition temperature of bath solution, annealing process were also involved and ZnO thin film was used as a seed catalyst by PVD method.

Besides that, in order to prepare the samples, the understanding of the characteristics of ZnO thin film has been studied so that the best properties can be optimized by some testing equipments used in this research. All the parameters were carried out according to types of testing being done, for example to observe the ZnO nanostructures images and diameter using field emission scanning electron microscopy (FESEM) attached with EDAX to determine the composition present in ZnO thin film. Other tests used was x-ray diffraction (XRD) equipment which is very important to analyse the crystal structure of ZnO nanostructure thin film as-prepared and annealed condition. UV-Vis spectrophotometer, photoluminescence and Raman spectroscopy were also used in this research to characterize the ZnO thin film that have optical properties which indicated that the light can transmit through the ZnO thin film by displaying the graphs curves.

1.5 THESIS ORGANIZATION

Chapter one briefly explains about introduction of the research carried out, problem statement, and objective of the research. Research scope is also presented in this chapter.

In chapter two, a brief review is presented from the contemporary works done by previous researcher, particularly on fundamentals on ZnO nanostructures properties, the synthesis methods used before to achieve the desired of nanostructures shapes. This chapter also includes the characterization investigated by some researchers such as morphology, crystal structure and also optical properties results. The comparison of ZnO nanostructures growth in low temperature and high temperature of deposition temperature by ECD method is also provided.

Chapter three introduces the methodology or experimental details used for this work. The preparation of ZnO thin film using ECD method is also discussed and the characterization process is also investigated in order to determine the parameters. All measurements used are mentioned in this chapter.

Chapter four presents the characterization of ZnO nanostructured. Results and discussion of the prepared samples using ECD method are also presented. The study includes thin film structural, morphological, and optical properties. The parameters for the study are two types of precursors used such as zinc chloride and zinc nitrate, different potential applied, and different deposition temperature of bath solution. An improvement of ZnO nanostructures thin film has also been made which involves the thermal annealing process using the oxygen atmosphere heat at 500°C in one hour. The next improvement is the growth of ZnO nanostructured for uniformity which uses ZnO as seed catalysis deposited by PVD method.

Finally, the thesis ends with some concluding results that achieved in this research through the best results are also presented. The recommendations part also includes for the future research in new technology that be expanded which are also discussed in chapter five.

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