LOW-TEMPERATURE GROWTH OF ZINC OXIDE STRUCTURES ON FLEXIBLE CONDUCTIVE SUBSTRATE: EFFECT OF NAOH AND $C_7H_8O_9$ PRESENCE IN SOL-GEL

ILI LIYANA KHAIRUNNISA BT KAMARDIN

A thesis submitted in
fulfilment of the requirement for the award of the
Degree of Master of Mechanical Engineering

Faculty of Mechanical and Manufacturing Engineering
Universiti Tun Hussein Onn Malaysia

FEBRUARY 2021

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been dully acknowledge

Ili Liyana

Student : ……………………………………………………………

ILI LIYANA KHAIRUNNISA KAMARDIN

Date : FEBRUARY 2021

Supervisor : ……………………………………………………………

PROF MADYA Ts DR. AINUN RAHMAHWATI BT AINUDDIN

To my beloved late father, late mother, brothers, and sisters.
Thank you for everything

ACKNOWLEDGEMENT

I would like to express my sincere appreciation to my supervisor, Prof Madya Ts. Dr Ainun Rahmahwati Bt Ainuddin @ Nordin, for the support given throughout this research.

Thank you for the cooperation given by technicians from the Science Material Laboratory, Mr Anuar Bin Ismail and Mr Tarmizi Bin Nasir. Appreciation also goes to everyone involved either directly or indirectly toward the compilation of this thesis. Last but not least, thanks to my family members for all their sacrifices for me.

ABSTRACT

ZnO is a unique material that exhibits semiconducting, piezoelectric, and pyroelectric multiple properties. ZnO nanostructures have drawn a widespread interest from researchers because of their multi-functional properties. The purposes of this study are to investigate the effects of adding sodium hydroxide and citric acid in the basic sol-gel on the formation of zinc oxide (ZnO) nanostructures via a chemical method. A ZnO sol was prepared by dissolving zinc acetate dehydrate (ZnAC) and diethanolamine (DEA) in deionized water (H_2O) and isopropanol (2-PrOH). The precursor solutions were spin-coated on the ITO/PET substrate and were dried at room temperature and pre-heated oven at 150°C for 3 minutes. Hot Water Treatment (HWT) was carried out at 70°C, 80°C, and 90°C for 8, 12, and 16 hours. X-ray diffraction (XRD) analysis recorded that (100) and (101) planes were formed as the preferred orientation samples with good quality and crystallization of the ZnO thin films. Based on Atomic Force Microscope (AFM) and Field Emission Scanning Electron Microscope (FESEM), HWT of 12 h immersed time was noticed as the optimum time for the growth of ZnO structures with the basic sol-gel solution. A 0.75 mol of NaOH and $C_6H_8O_7$, respectively, was dropped in the basic solution for the second part of this study. The HWT was carried out at 90°C for 8, 12, and 16 hours. The presence of NaOH recorded higher intensity with ZnO sheet structure in a flower bud shape. The size of the structures approached nano-size. The presence of NaOH and $C_6H_8O_7$ has changed the ZnO dimension from 1D to 2D. The ZnO 1D rod structures and 2D sheet structures can be used in LED, solar cells, photodetectors, gas sensor, field emitter, and photovoltaic devices.

ABSTRAK

ZnO ialah suatu bahan unik yang mempamerkan sifat semikonduktor, piezoelektrik, dan piroelektrik. ZnO berstruktur nano telah menarik minat ramai penyelidik kerana sifatnya yang mempunyai pelbagai fungsi. Tujuan kajian ini adalah untuk mengkaji kesan penambahan natrium hidroksida dan asid sitrik dalam sol-gel asas terhadap pembentukan ZnO berstruktur nano melalui kaedah kimia. Larutan jel ZnO disediakan oleh zink asetat dihidrat (ZnAC) dan dietanolamin (DEA) dalam air deionisasi (H2O) dan isopropanol (2-PrOH). Larutan jel disalut pada substrat ITO/PET melalui kaedah putaran dan dikeringkan pada suhu bilik dan ketuhar yang telah dipanaskan pada suhu 150°C selama 3 minit. Rawatan air panas (HWT) dilakukan pada suhu 70°C, 80°C, dan 90°C selama 8, 12, dan 16 jam. Analisis difraksi sinar-X (XRD) mencatatkan satah (100) dan (101) dibentuk sebagai sampel orientasi pilihan dengan kualiti yang baik dan penghabluran filem nipis ZnO. Berdasarkan mikroskop daya atom (AFM) dan mikroskop elektron pengimbas pelepasan medan (FESEM), rawatan air panas yang direndam selama 12 jam ialah masa optimum untuk pertumbuhan struktur ZnO dengan larutan asas jel. Larutan 0.75 mol NaOH dan $C_6H_8O_7$ dimasukan ke dalam larutan asas jel untuk bahagian kedua kajian ini. Kehadiran NaOH mencatatkan intensiti yang lebih tinggi dengan struktur lembaran ZnO dalam bentuk putik bunga. Ukuran struktur juga menghampiri ukuran nano. Kehadiran NaOH dan $C_6H_8O_7$ dalam larutan jel telah menukarkan dimensi struktrur ZnO dari 1D kepada 2D. Struktur batang ZnO 1D dan struktur lembaran 2D dapat digunakan dalam LED, sel suria, pengesan foto, sensor gas, pemancar medan, dan peranti fotovoltaik.

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LIST OF SYMBOLS AND ABBREVIATIONS

°	degree
°C	degree Celsius
1D	one dimensional
2D	two dimensional
2-ProH	isopropyl alcohol
2θ	2 theta
3D	three dimensional
A	ampere
Å	angstrom,
a_o	linear expansion
AFM	atomic force microscopy
Al	aluminium
Al_2O_3	aluminium oxide
AlN	aluminium nitride
B. Eng.	Bachelor of Engineering
C_1	concentration of starting solution
C_2	concentration needed
$C_6H_8O_7$	citric acid
CBM	conduction band maximum
Ce	cerium
cm	centimeter
cm^2/Vs	electron mobility unit
CO	carbon monoxide
c_o	coefficient
CO_2	carbon dioxide
CuKα	Copper Kα

D	diameter
DEA	diethanolamine
DSSC	dyed-synthesized solar cells
dx	infinitesimal change in x
ERT	ekonomi rumah tangga
EDX	energy dispersive x-ray spectroscopy
eV	electronevolt
FESEM	field emission scanning electron microscope
FET	field emission transistor
FKMP	Fakulti Kejuruteraan Mekanikal & Pembuatan
FTO	fluorine-doped tin oxide
g	gram
GaN	galium nitrade
Gpa	gigapascal
H	hydrogen
h	hour
h	final thickness
H_2O	water
Hons	Honors
HWT	hot water treatment
Hz	hertz
ITO	indium tin oxide
kV	kilovolt
L	length
l	liter
LED	light emitting diodes
m	evaporation rate of solvent
M. Eng.	Master of Engineering
mA	milliampere
MACC	Malaysian Anti-Corruption Commission
meV	millielectronevol
min	minute
ml	milliliter

mol	molarity
MOVPE	metal-organic vapor phase epitaxy (MOVPE)
NaCl	sodium chloride
NaOH	sodium hydroxide
NGO	Non-Government Organization
nm	nanometer
O_2	oxygen
OH	hydroxide
PC	polycarbonate
PES	polyester sulfone
PET	polyethylene terephtalate
pH	potential of hydrogen
PMMA	poly(methyl methacrylate)
pxl	pixel
RMS	root mean square
rpm	rotation per minute
R_q	RMS roughness
RT	room temperature
$\int$	integral
S_1	speed 1
S_2	speed 2
sec	second
SEI	secondary electron imaging
SEM	scanning electron microscope
Si	silicon
SiO_2	silicon dioxide
t_1	time 1
t_2	time 2
TiO_2	titanium oxide
t_{pr}	pre-heat time
UTHM	Universiti Tun Hussein Onn Malaysia
UV	ultra violet

V_1	volume 1
V_2	volume 2
XRD	x-ray diffraction
$y(x)$	variation of height
Zn	zinc
$Zn(NO_3)_2.6(H_2O)$	zinc nitrate
ZnAc	zinc acetate
ZnO	zinc oxide
ZrO_3	zirconium oxide
β	beta
δ	delta
η	viscosity
θ	theta
λ	wavelength
μm	micrometer
ρA	volatile solvent density
ρA_o	initial value of ρA
ω	angular speed
Ω/sq	ohm per square, sheet resistance

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

This thesis is organized into five chapters. Chapter 1 presents the Introduction, Chapter 2 discusses the Literature Review, Chapter 3 describes the Methodology, Chapter 4 states the Results and Discussions, and Chapter 5 presents the Conclusion and Recommendations.

Chapter 1 begins with the introduction of the thesis. It consists of 5 subchapters that cover the background of the study, problem statement, the objectives, scope of the study, and the significance of the study. Brief descriptions of other chapters will be discussed in each corresponding chapter.

1.1 Background of the study

ZnO is a unique material that exhibits semiconducting, piezoelectric, and pyroelectric multiple properties. ZnO has been classified into three groups with various structures. Nanowires [1], [2], nanobelts [3], [4], nanorods [5], [6], [7], [8] and nanotubes [9], [10], [11], nanoring [12], [13], and nanocombs [14], [15] are known as one-dimensional (1D). Nanosheet [16], [17], [18], [19], nanoflakes [20], [21], [22] [23], nanodisks [24], [25], nanoplates [26], [27], and nanowalls [28], [29] are known as two-dimensional (2D). Nanocages [30], [31], nanopropeller [32], [33], nanoflowers [24], [34], [35], [36], [37], and nanohelix/nanospring [38], [39] are classified as three-dimensional (3D). ZnO nanostructures have drawn a widespread interest from researchers because of their multi-functional properties, leading to possible applications in existing and emerging electronic and optoelectronic industries [40], [41].

Table 1.1 shows the summary of previous researches on ZnO application according to their dimensional structures. From the table, ZnO 1D nanostructures have been extensively studied for device applications followed by ZnO 2D nanostructures. Based on existing studies, ZnO 1D and 2D nanostructures have been widely produced by using a simple and facile method [37], [42], [43], [44], [45], [46].

Table 1.1: Summary of ZnO applications.

Structures	Applications	References
1D	dyed-synthesized solar cells (DSSC)	[1], [47], [48], [49], [50]
	light-emitting-diodes (LED)	[51]
	flexible field-effect-transistors (FET)	[2]
	gas sensors	[13], [52]
	UV protection films	[53]
	photovoltaic devices	[54]
	solar cells	[55], [56]
	piezoelectric	[57]
2D	photodetector	[58]
	gas sensor	[24], [28], [59]
	solar cells	[44]
	nanogenerator	[60]
3D	gas sensor	[30]
	DSSC	[61]

Hierarchical ZnO nanostructures with multi-scale configurations consisting of ZnO nanosheets and nanorods were demonstrated by Qiu, Zhang, Liao, Qiu, Huang, and Zhang (2011) to achieve a higher internal surface area for photoelectrodes [62]. Using a solid-vapor phase thermal sublimation technique, ZnO has been synthesized under a specific growth condition. These unique nanostructures clearly show that

ZnO is probably the richest family of nanostructure among all materials in properties and structure. Nanostructure could have a novel application in the transducer, biomedical science, sensors, and optoelectronics because it is bio-safe [63].

Despite the successful formation of the desired aligned nanostructures, research efforts continue to focus on the formation of ZnO nanorods and mixtures of nanostructures, like nanorods and nanosheets, through viable, cost-effective, and near-room temperature processes. The enrichment of the surface region of the 1D nanostructure is important because the hierarchical and complex ZnO nanoarchitecture has stimulated a considerable interest in the 2D and 3D structures. When the two structures can be made to co-exist on the same substrate, it is expected that unique properties that cannot be found in mono-morphological structures could be obtained [64].

Hydrothermal method [65], chemical vapor deposition [66], molecular beam epitaxy [67], Hot Water Treatment (HWT) [68], and laser ablation [69] have been reported as a ZnO nanostructure synthesis method. The HWT method has been announced as a facile and low-cost method on the formation of ZnO nanostructure.

Formation of ZnO by HWT is possible at a low temperature of 90°C which will give an advantage to the development of flexible optoelectronic devices that use a substrate with low thermal stability. Other than that, HWT method can avoid contamination of the specimen due to the usage of deionized water to stimulate the formation of nanosheet, nanowire, nanorods, nanostar-like, and nanoneedle-like [70].

1.2 Problem statement

There are various types of coating methods used in ZnO thin film synthesizing process, especially for solar cell applications. A wide range of deposition technologies have been chosen for most of the oxide coating process. However, chosen deposition technologies are influenced by nature and area of the surface to be coated, the growth kinetics of crystalline structure, the source of material utilization efficiency of the process, deposition rate, and the availability of low-cost source materials among others [71].

The solution-based coating or known as sol-gel coating is one of the versatile methods to produce thin films because it is inexpensive, simple, covers a large deposition area, and produces uniform film thickness [72]. The sol-gel method also allows hybridization of organic, metallic, and inorganic materials at low temperature [73]. Spin and dip sol-gel coating is the most commonly used method for its simplicity and low cost compared to other coating methods. That method also requires a pre-heating process under 150°C of pre-heat temperature. A pre-heat temperature exceeding 150°C not only changes the shape, but also the structure of the substrate, and flexible substrate cannot bear temperature more than 150°C. There are insufficient studies on the optimum pre-heat temperature and time for the flexible substrate found.

1.3 Objectives

The objectives of this research are:

i. To investigate the effect of immersed time synthesis of ZnO on ITO/PET flexible substrate using hot water treatment.

ii. To investigate the effect of low-temperature synthesis of ZnO on ITO/PET flexible substrates.

iii. To improve the growth of ZnO structures on ITO/PET flexible substrate by adding 0.75 mol of NaOH and $C_6H_8O_7$ as the presence of alkaline and acid in the precursor solution.

The purposes of this study are to investigate and control the formation of ZnO structures via chemical method, which is sol-gel assisted by hot water treatment. The interest in flexible optoelectronic devices has gained attention from the research community. However, reports on flexible devices are very limited, hence the research findings on architecture of ZnO nanostructure formation at low temperature could be applied on flexible substrates with low thermal stability.

1.4 Scope of the study

The scopes of this study are:

i. Basic sol-gel solutions obtained by using DEA, ZnAc, H_2O, and 2-PrOH with the ratio of 1:1:1:20.

ii. ITO/PET flexible substrate coated by spin coating method at 300 rpm for 10 seconds and 400 rpm for the next 20 seconds.
iii. Samples were pre-heated in an oven at 100°C for 3 minutes.
iv. Basic sol-gel samples were hot water treated at 70°C, 80°C, and 90°C for 8, 12, and 16 hours by using deionized water.
v. 1 ml each of 0.75 mol of NaOH and $C_6H_8O_7$ was added into separate ZnO sol-gel solution. HWT process was maintained at 90°C for 8, 12, and 16 hours by using deionized water.

1.5 Significance of the study

Research on growth of ZnO low-temperature nanostructure on flexible conductive substrates for device fabrication will contribute in the thin film industry as we focus its application on uneven device surface. The flexible thin film would be easily attached to different shapes of surface, and its lightweight property would enable it as a mobile power source for portable devices. Flexible thin films are important not only to reduce cost in manufacturing thin films, but also significantly enhance life’s conveniences.

CHAPTER 2

LITERATURE REVIEW

This chapter will discuss the literature review related to this study. This chapter consists of five subchapters; thin film, seed layer, ZnO properties, ZnO nanostructure synthesis, and flexible conductive substrate.

2.1 Thin film

Adachi and Wasa (2012) have defined thin film as a low-dimensional material produced by condensing, one by one, and atomic/molecular/ionic species of matter [74]. The thickness is typically less than several microns [75]. Thin films have been used for more than a half-century in making instrument hard coatings, optical coatings, electronic devices [76], [77], and decorative parts. The thin film is a traditional well-established material technology. However, thin film technology is still being developed until today due to its potential in the twenty-first-century development of new materials such as nanometer materials and/or man-made superlattices.

Thin film materials and devices also promise on minimization of toxic materials since the quantity used is limited only to the surface or thin film layer [78]. Thin film processing also saves energy in production and is considered an environmentally friendly material technology for the next century. Thin film technology is both old and current key material technology [79].

Thin film materials and synthesis processes via sol-gel facilitated by HWT have been reviewed in several publications. Tadanaga (2006) prepared an Al_2O_3

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