

CHARACTERIZATION OF NANOSTRUCTURES ZnO SYNTHESIZED
THROUGH HYDROTHERMAL METHOD

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For my

Beloved parents

Mior Idris Bin Jamaludin and Aminah Binti Abd Rahman

The reason of what I become today
Thanks for great support and continuous care

Dearest siblings

Aniyah, Arifah and Aiman

The inspiration of what I do today
I am really grateful to have all of you

Lovely buddies

Thanks for the each support and joy



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ABSTRACT

ZnO nanostructures can be derived using a variety of techniques. Using hydrothermal synthesis, ZnO nanostructures can be produced easily on a large scale due to the low temperature involved. Among the factors that influence the crystallinity of ZnO nanostructures are types of alkaline solution, the alkaline pH value used and the application hours of the hydrothermal process. This research focuses on the fabricated ZnO nanostructures via hydrothermal synthesis and the effects of alkaline solution on the morphology of ZnO nanostructures. Distilled water was mixed with three types of alkaline which are NaOH, KOH and LiOH solutions in 3 different pH values. The hydrothermal process was conducted using three different time periods which are 6, 12 and 24 hours. XRD analysis was done to identify the phase and crystallinity of ZnO nanostructures. Morphology and surface roughness analysis were characterized using FESEM and AFM to observe the nanostructures growing on ZnO thin films while current against voltage testing was done to identify the resistivity of ZnO nanostructures using a 2-probe point analyzer. All of these analyses were performed on the growth of ZnO nanostructures after the hydrothermal process. The results revealed that the addition of KOH solution as a precursor provides the best nanostructure properties over other alkaline solutions. The most suitable time period required to produce the best ZnO crystalline structure is 24 hours while the perfect pH value that allows the formation of ZnO nanostructures is 12.

ABSTRAK

Umumnya, nanostruktur bagi ZnO boleh dihasilkan melalui pelbagai teknik. Melalui kaedah hidrotermal, nanostruktur bagi ZnO boleh dihasilkan dengan banyak dan prosesnya ringkas kerana melibatkan penggunaan suhu yang rendah. Antara faktor yang mempengaruhi pertumbuhan nanostruktur ZnO yang baik ialah penambahan jenis larutan alkali, kepekatan pH alkali yang digunakan dan juga masa proses hidrotermal dijalankan. Kajian ini menumpu kepada fabrikasi nanostruktur bagi ZnO melalui kaedah hidrotermal dan kesan pengaruh larutan alkali keatas morfologi kerajang nipis Zn. Air suling telah dicampur bersama 3 jenis alkali yang berbeza yang mana mempunyai 3 kepekatan pH yng berbeza. Kerajang Zn telah dijalankan proses hidrotermal selama 6, 12 dan juga 24 jam. Analisis XRD dijalankan bagi mengetahui fasa dan kehabluran bagi nanostruktur yang terhasil. Analisis morfologi dan juga analisis kekasaran permukaan yang dijalankan oleh FESEM dan AFM bertujuan untuk melihat struktur nano ZnO yang terhasil pada kerajang Zn. Ujian arus melawan voltan yang dijalankan oleh *2-point probe* bertujuan untuk mengetahui nilai keringtangan yang wujud bagi nano struktur ZnO. Kesemua analisis ini dijalankan pada kerajang ZnO selepas proses hidrotermal dijalankan. Larutan alkali yang menghasilkan nanostruktur ZnO yang baik adalah larutan alkali jenis KOH. Manakala masa yang terbaik untuk menghasilkan struktur hablur pada kerajang ZnO ialah sebanyak 24 jam dan kepekatan alkali yang sesuai digunakan adalah pH 12.

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LIST OF SYMBOLS

°C	-	Degree celcius
%	-	Percent
pH	-	Pontential Hydrogen
ZnO	-	Zinc Oxide
TCO	-	Transperent and Conductive Oxide
PL	-	Photoluminescences
ITO	-	Indium-Tin Oxide
TiO ₂	-	Titanium Dioxide
ZAH	-	Zinc Acetate Hydrate
NaOH	-	Sodium Hydroxide
KOH	-	Potassium Hydroxide
LiOH	-	Lithium Hydroxide
HCl	-	Hydrochloride
XRD	-	X-ray Diffractometer
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier Transform Infrared Spectroscopy
nm	-	Nanometer
EtOH	-	Ethanol
I _{sc}	-	Short Circuit Current
V _{oc}	-	Voltage-Operated Channels

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Zinc Oxide (ZnO) has a wide number of properties which has gained considerable attention from researchers over the past few years. ZnO is a popular material used in semiconductor research and this was mentioned back in 1945 (Gomez & Tigli, 2012). World-wide use of ZnO that has 9 % of metallic zinc is more than 1.2 million tonnes per year (International Zinc Association, 2011). Due to its unique chemical properties and structure, ZnO is increasingly being used in the production of electronic devices. The applications of ZnO are not only limited to the engineering field, but also the pharmaceutical industry, cosmetic and food packaging industry.

There are wide applications of ZnO in hybrid solar cells and organic solar cells due to its low cost, ease of synthesis, non-toxicity, high stability and good optoelectronic properties (Huang, Yin, & Zheng, 2011). Doped ZnO thin films are transparent electrodes for solar cells. Solar cells require a transparent and conductive oxide (TCO) thin film that can extract the electrical current and allow the light to enter the absorber layers (Tadatsugu, 2005). ZnO is not only highly transparent but also highly conductive and strongly suitable to be a TCO candidate.

There are two types of synthesis methods to obtain the ZnO nanostructure. The ways are solution phase synthesis and gas phase synthesis. For solution phase synthesis, normally the aqueous solution is used and the process is referred to as hydrothermal growth process. Baruah & Dutta(2009) in their research said that solution phase synthesis processes consist of several methods. First, Zinc Acetate Hydrate (ZAH) is derived from nano-colloidal sol-gel route, ZAH in alcoholic solutions with Sodium Hydroxide (NaOH), template assisted growth, spray pyrolysis for growth of thin films and electrophoresis. Due to the variety in methods, the

structure and look of ZnO produced could be different. The best structure of ZnO is nanowire because of its good performance in electronics, optics and photons field (Yangyang *et al.*, 2012).

1.2 Statement of Problem

Basically, ZnO nanostructures can be derived using a variety of techniques. Based on Segovia *et al.*, (2012) , hydrothermal synthesis or wet chemistry techniques are simple and proved to be efficient methods to obtain nanostructure thin films on a large scale. Besides that, Yangyang *et al.*, (2012) said that hydrothermal synthesis has been used for the synthesis of 1-D nanostructures that are useful in different fields such as Dye-Sensitized Solar Cells due the unique electrical properties. Nanostructures that are categorized in 1-D are nanowires, nanorods, nanofibres, nanobelts and nanotubes. The growth of ZnO nanostructures via hydrothermal synthesis can be controlled by alkaline reagents, initial solution pH, and growth duration. All of these parameters affect the nanostructures of ZnO and diversifies the properties of ZnO.

Research on ZnO nanostructures produced based on different parameters will be emphasized in this study. The best parameters to produce ZnO nanostructures with electrical properties based on solar cell application through hydrothermal synthesis will be identified.

1.3 Objectives

- 1) To fabricate the nanostructure of ZnO via hydrothermal synthesis method.
- 2) To study the effects of different types of alkaline solution on the morphologies of the synthesized ZnO nanostructures.

1.4 Scope of Study

- 1) Zinc foil (99.9% purity) was used as substrate and solid reagent.
- 2) Zinc foils were produced via hydrothermal synthesis in different alkaline solutions such as NaOH, KOH and LiOH.
- 3) Hydrothermal synthesis by an autoclave at 120°C for 6, 12 and 24 hours.

- 4) Alkaline concentrations of pH 10 and 12 were used for formation control of ZnO nanostructure.
- 5) The crystallinity and phases of ZnO nanostructures were characterized by X-ray Diffractometer (XRD).
- 6) Surface morphology of the ZnO nanostructures with different alkaline concentration was characterized by Field Emission Scanning Electron Microscopy (FE-SEM).
- 7) The surface roughness of ZnO nanostructures was measured by Atomic Force Microscopy (AFM).
- 8) 2-point probe was used to measure the current-voltage (I-V) for ZnO nanostructures.



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CHAPTER 2

LITERATURE REVIEW

2.1 Introductions

Thin films are very thin layers of substances that are used to support materials. It is common in solar energy applications today to generally use thin films on solar panels to absorb energy from the sun. To do so, the photovoltaic material will be deposited in thin layers on substrates such as glass, plastic or metal. Thin film solar cells have several differences as compared to traditional solar cells like silicon whereby it performs as a semi-conductor. Thin films are considered second generation solar cells after silicon solar cells because they are made from semiconductor materials that are a few micrometers in thickness.

Thin films will be deposited on various materials to produce nanostructures. The application of nanoscale materials will be able to convert solar energy with higher efficiency and produce low-cost devices (Beard, Luther, and Nozik, 2014). This indirectly revolutionises solar cell application. Nanostructures layered on thin film have several advantages. Based on the review made by Sagadevan (2013), there are three advantages of nanostructures in solar energy application. First advantage being, the absorption of nanostructures are more effective than the absorption of actual film thickness due to multiple reflections. Secondly, the electrons generated by light travels a much shorter path avoiding losses. Lastly, the size of nanoparticles allows more flexibility in the absorption of solar cells.

ZnO polar surfaces are actually very stable and include many different nanostructures. The nanostructures provide many advantages for several applications, especially for catalyses and surfaces. The surface is easier to modify and provides improved solar cell performance when it is running (Chou *et al.*, 2007). ZnO also has a band gap that is the same as TiO₂ while having much higher electron

mobility. Figure 2.1 shows a band position of several semiconductors in aqueous electrolyte at pH 1. The greater gap allows higher breakdown voltage and larger ability to sustain electric fields (Baruah and Dutta, 2009).

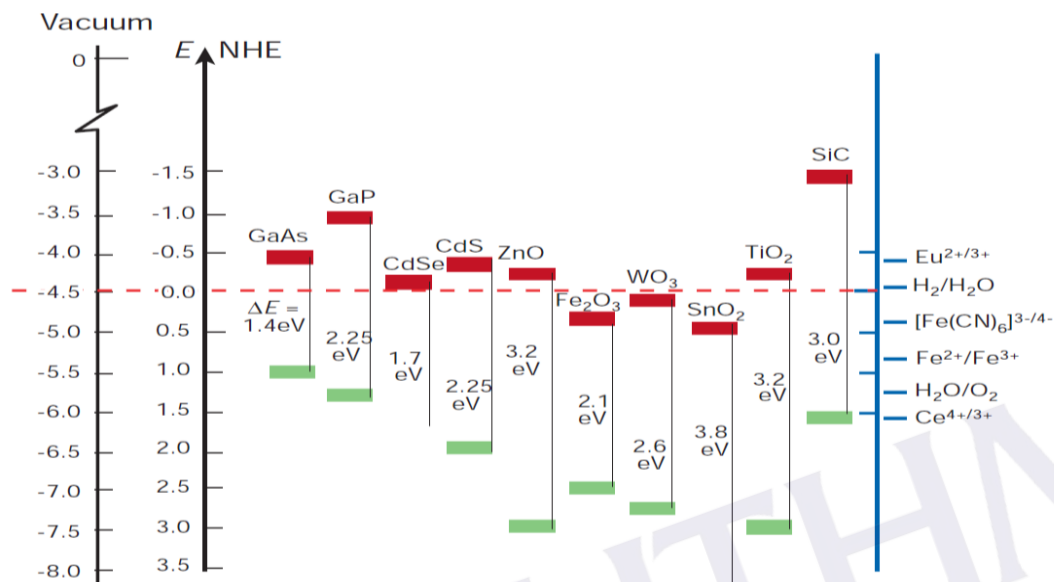


Figure 2.1: Band Position of Several Semiconductor in Aqueous Electrolyte at pH 1 (Chou *et al.*, 2007)

One dimensional nanostructure of ZnO is more efficient to carry and transport with decreased surface defects, grain boundaries, disorders, and discontinuous interfaces (Chen *et al.*, 2010). ZnO also has properties like transparent conducting oxides (TCO). Usually, the most widely used TCO is indium-tin oxide (ITO). However, an active search for alternative materials is underway because of the high processing cost. The applications of ZnO as TCO is well-suited because of its low cost and non-toxicity (Noriega *et al.*, 2010). Thus, it makes a popular TCO in the application of solar cells. It is widely used in applications of solar cells because of their optical transmission in the visible and electrical conductivity. Ridhuan *et al.*, (2012) in their paper said that, the seeding of substrates by hydrothermal method has better controlled morphology and growth direction of ZnO nanostructures. Table 2.1 shows the ZnO nanostructured properties.

Table 2.1: ZnO nanostructures properties (Fan & Lu, 2005)

Properties	Values
Lattice Parameters (T= 300K)	a=b=3.25 Å c=5.21 Å u=0.348 c/a=1.593-1.6035
Density	5.606 gm/cm ³
Melting Point	2248 K
Stable Crystal Structure	Wurtzite
Dielectric Constant	8.66
Refractive Index	2.008
Band Gap (E _g)	3.37 eV (direct)
Exciton Binding Energy	60 meV
Electron/ Hole Effective Mass	0.24 m _o / 0.59 m _o
Hole Mobility (300K)	5-50 cm ² /Vs
Electron Mobility (300K)	100-200 cm ² /Vs

2.2 Hydrothermal Synthesis

Hydrothermal synthesis is the technique of fabricating materials from low temperature aqueous solution in high vapour pressure and a synthesis process of single crystals. This method will save energy and is more environmental-friendly because the reaction is done in closed system conditions. Moreover, this synthesis is also able to fabricate single crystals in low temperatures. The main advantage of synthesising in low temperatures is that it is simple and energy efficient (Komarneni, 2003). To control the size and shape of the nanophases, this method is more suitable.

Hydrothermal synthesis can be done through two methods: Conventional Hydrothermal and Microwave Hydrothermal. Conventional Hydrothermal synthesis uses cold seal vessels and Parr vessels. Cold seal vessels control pressure and temperature, while Parr vessels only control temperature with precision. Parr vessels will not control the pressure parameters. Hydrothermal process by microwave however, gives other advantages when compared to conventional hydrothermal method. Komarneni (2003) in his study said, reaction system by microwave has more rapid kinetics than conventional hydrothermal. The rutile crystallisation happens in between 0.5 to 2 hours in 0.5 to 3 M titanium oxychloride solutions, while the reaction through conventional hydrothermal takes 3 days to be completed.

In a study done by Kharisov, Kharissova, and Méndez (2012), they showed the morphology control of ZnO nanostructures by microwave hydrothermal. ZnO nuclei will transform into nanorods by preferential c-axis [002] with oriented 1D growth. Nanowires that form from nanorods become nanospindles because of the

increase in diameter and local dissolution. The nanorods can also become nanodendalions from the multiple growths of nanorods. Crystal growth along the [002] direction becomes nanoslices due to quasi 1D growth. Finally, nanothruster vanes form due to assembled growth of nanoslices. Figure 2.2 shows the shape-controlled synthesis of ZnO nanorod, nanowire, nanothruster vanes, nanodendalions and nanospindles using the microwave hydrothermal method.

From the researches done, we now know that ZnO materials do have important properties like photoluminescence and photocatalysis. The nanostructures that give good performances in photoluminescence are known as nanoflowers (Lai *et al.*, 2011). This structure is a special three dimensional nano-ZnO. Between the variables that can be controlled to develop good nanostructures are: types of alkaline solution, temperature, hydrothermal reaction time, and difference in pH value.

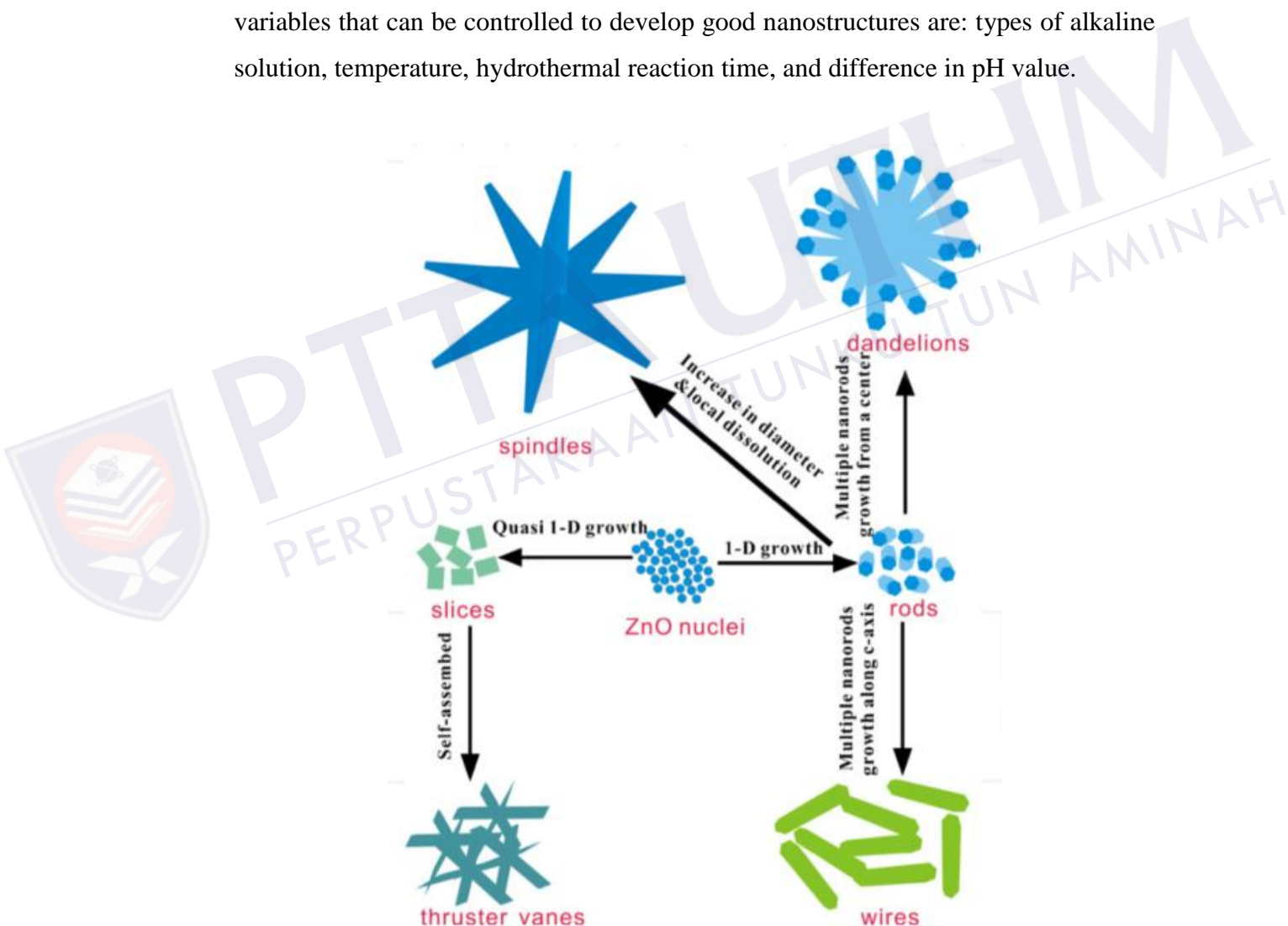


Figure 2.2: The shaped controlled synthesis of ZnO using microwave hydrothermal (Kharisov *et al.*, 2012)

2.3 Effects of Different Alkaline

The use of different alkaline solution in hydrothermal synthesis will give a result that is non-toxic, environmentally beneficial, easily available, and relatively inexpensive chemical. In the research by Ekthammathat *et al.*, (2014), it shows that alkaline solution helps in the crystallisation process and generate nanostructure like rod, pencil and star. The ZnO is synthesised by NaOH, LiOH and NH₄OH. Using these alkaline solutions result in a ZnO thin film that is very sharp in XRD pattern which indicates that product has good crystalline structure. Figure 2.3, shows that all diffraction patterns can be categorised as hexagonal wurtzite structures. ZnO that is synthesised in NaOH solution has the highest diffraction peak at 34.45°. However, ZnO synthesized using LiOH and NH₄OH solutions do have strong diffraction peaks on (002) and (101) planes in relatively intensified diffractions.

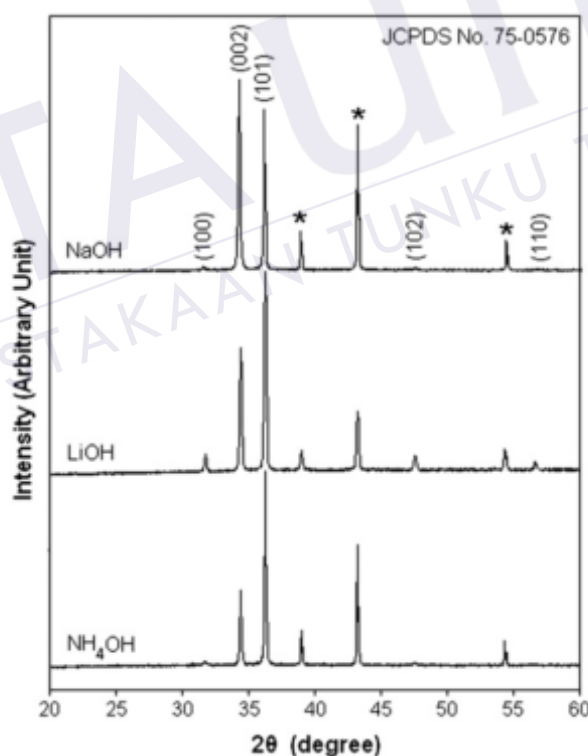


Figure 2.3: XRD patterns of ZnO synthesized by NaOH, LiOH and NH₄OH alkaline solutions (Ekthammathat *et al.*, 2014).

Ni *et al.*, (2005) also conducted a research on the preparation of ZnO nanorods that grows in powder form. In his research, KOH solution was mixed with ZnCl₂ to produce the ZnO powder through the hydrothermal process. The result of

XRD shows a strong diffraction peak at (101) plane and it directly shows that this material has good crystallinity and size. By using KOH solution, the sizes of the structures become more homogeneous and have a mean size of about 50 nm x 250 nm.

Based on the study by Pei *et al.*, (2010) on oxidation of Zn substrate by distilled water however, the highest peak of intensity by XRD are also shown on planes (101) and (002). The strong diffraction peaks on the planes were suggested to have a preferential growth direction even through the use of distilled water as precursor. The XRD pattern is shown in Figure 2.4.

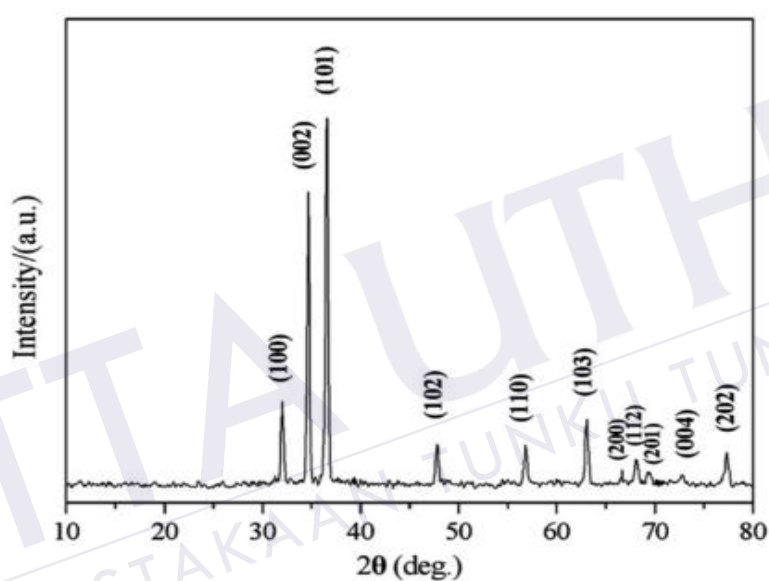


Figure 2.4: XRD pattern through oxidation of Zn substrate by distilled water (Pei *et al.*, 2010)

The use of a variety of alkaline as precursor is able to give different thickness in ZnO layer growths. The thicker the ZnO layers might be due to the low value of conversion efficiency. This statement is based on the study conducted by Baviskar, Tan, Zhang, and Sankapal (2009), where the value of voltage is 428 mV and the photovoltaic conversion efficiency is 0.34 %. Figure 2.5 shows the result of current density against voltage (J-V) from the study. Besides that, it is also found that the thickness value is indirectly caused by the increase of the resistivity (Shariffudin, Salina, Herman, and Rusop, 2012).

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