FABRICATION AND CHARACTERIZATIONS OF POROUS ZINC OXIDE THIN FILMS

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FABRICATION AND CHARACTERIZATIONS OF POROUS ZINC OXIDE THIN FILMS

by

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LIST OF SYMBOLS

ω	Angular frequency
$\varepsilon_{xx}(\omega)$	Dielectric tensors along the *x* direction
$\varepsilon_{yy}(\omega)$	Dielectric tensors along the *y* direction
$\varepsilon_{zz}(\omega)$	Dielectric tensors along the *z* direction
ε	Dielectric tensor component
m	Independent components
n	Independent components
$\perp$	Perpendicular component
$\parallel$	Parallel component

LIST OF ABREVIATIONS

AC	Alternating current
AFM	Atomic force microscopy
Ag	Argentums
Al	Aluminum
Al_2O_3	Sapphire
Al_2O_3	Alumina
Ar	Argon
Au	Gold
Cu	Copper
CVD	Chemical vapor deposition
DC	Direct current
DLE	Deep level emissions
EBL	Electron beam lithograph
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared
FWHM	Full width half maximum
GaN	Gallium nitride
GaP	Gallium phosphate
HCl	Hydrochloric acid
HMT	Hexamethylenetetramine
InN	Indium nitride
IR	Infrared
ITO	Indium tin oxide
KOH	Potassium hydroxide
LO	Longitudinal optical
NaCl	Sodium chloride
NBE	Near band edge emissions
NH_4Cl	Ammonium chloride
n-Si(111)	N-type silicon with (111) preferred orientation
O_2	Oxygen
OH^-	Hydroxide ions

PL	Photoluminescence
PLD	Pulsed laser deposition
PS	Polystyrene spheres
Pt	Platinum
RF	Radio frequency
SEI	Semiconductor-electrolyte interface
SEM	Scanning electron microscope
Si	Silicon
SiC	Silicon carbide
SiO_2	Silicon dioxide
TO	Transverse optical
UV	Ultraviolet
XRD	X-ray diffraction
Zn	Zinc
$Zn(NO_3)_2$	Zinc nitrate
$Zn(NO_3)_2$ 6H2O	Zinc nitrate hexahydrate
Zn^{2+}	Zinc ions
$ZnCl_2$	Zinc chloride
ZnO	Zinc oxide

FABRIKASI DAN PENCIRIAN FILEM NIPIS ZINK OKSIDA BERLIANG

ABSTRAK

Objektif utama projek ini adalah untuk mengkaji fabrikasi filem nipis ZnO berliang melalui keadah punaran elektrokimia dengan bantuan cahaya ultra ungu dan untuk menciri morfologi permukaan, struktur keratan dan ciri-ciri optik sampel berliang. Di samping itu, penentuan keliangan dan ketebalan bagi filem nipis ZnO berliang yang terpilih dengan menggunakan spektrum pantulan infremerah (IR) dan teori medium berkesan juga ditunjukkan.

Dalam kajian ini, tiga eksperimen fabrikasi ZnO berliang telah dijalankan. Dalam eksperimen ini, kesan kepekatan larutan pemunar, keupayaan punaran dan masa punaran ke atas fabrikasi ZnO berliang telah dikaji secara berasingan. Filem nipis ZnO berliang yang difabrikasi telah dicirikan dengan mikroskopi elektron pengimbas (SEM), spektroskopi fotoluminasi (PL) dan spektroskopi inframerah transformasi Fourier.

Keputusan SEM menunjukkan ZnO berliang yang berbentuk seperti anak bukit telah berjaya diperoleh dalam kajian ini. Imej keratan SEM pula menujukkan kewujudan punaran yang didominasi oleh punaran ansiotropik semasa punaran elektrokimia filem nipis ZnO. Selain itu, keputusan pencirian PL menunjukkan peningkatan keamatan puncak pancaran pinggir jalur dalam kebanyakan sampel. Keputusan pantulan IR pula menunjukkan satu bonggol resonans tambahan di kawasan reststrahlen yang disebabkan oleh struktur permukaan seperti anak bukit. Melalui padanan spektrum pantulan IR, persetujuan yang baik di antara spektrum teori dan ekperimen diperoleh.

Projek ini telah membawa kepada permulaan kajian punaran elektrokimia filem nipis ZnO untuk aplikasi peranti. Selain itu, keputusan yang diperoleh dalam kajian ini juga telah menyumbang kepada penambahan ilmu pengetahuan tentang kelakuan punaran filem nipis ZnO dan ciri-ciri struktur dan optiknya. Ini boleh dijadikan sebagai satu rujukan untuk kajian punaran elektrokimia filem nipis ZnO pada masa depan.

FABRICATION AND CHARACTERIZATIONS OF POROUS ZINC OXIDE THIN FILMS

ABSTRACT

The main objectives of this project are to study the fabrication of porous ZnO thin films by using ultraviolet light assisted electrochemical etching method and to characterize the surface morphologies, the cross sectional structure and the optical properties of the porous samples. In addition, the determination of porosities and thicknesses of selected porous ZnO thin films with the use of infrared (IR) reflectance spectra and effective medium theories is also demonstrated.

In this work, three fabrication experiments of porous ZnO are carried out. In these experiments, the effects of etchant concentration, etching potential and etching time on the fabricated porous ZnO thin films are investigated separately. The fabricated porous ZnO thin films are characterized by using scanning electron microscopy (SEM), photoluminescence (PL) spectroscopy and Fourier transform infrared spectroscopy.

SEM results revealed that hillock like porous ZnO thin films are successfully obtained throughout this study. The cross sectional SEM images also indicated the occurrence of anisotropic dominated etching during the electrochemical etching of ZnO thin films. Besides that, the PL characterization results showed that there is enhancement of near band edge emission peak in most of the porous samples. IR reflectance results revealed that an additional resonance hump in the reststrahlen region induced by the hillock like porous structure. Through the fitting of the IR reflectance spectra, good agreement between the theoretical and experimental spectra is obtained.

This project has led to the initiation of the study of electrochemical etching of ZnO thin films for the devices applications. Besides that, the results obtained in this study have also contributed to the additional of knowledge in the etching behavior of ZnO thin films as well as their structural and optical properties. These can become a reference for the future study in the electrochemical etching of ZnO thin films.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Unique properties of zinc oxide (ZnO) such as wide band gap energy and high binding energy (Shin et al., 2004) as well as its potential application in various devices such as solar cell (Zhang et al., 2009; Cheng et al., 2008) , sensors (Gupta et al., 2010), light emitting devices (Tsukazaki et al., 2005; Choi et al., 2009)have earned intense attention within the research community. The involvement of ZnO in the semiconductor devices fabrication progressively increases when the nanostructure, microstructure and porous ZnO fabrication techniques, also known as surface patterning techniques, are developed. Till today, various surface patterning techniques of ZnO material have been developed for various applications such as sensors, solar cells and light emitting devices. Some of these examples are chemical vapor deposition (Cheng et al., 2008), unbalance magnetron sputtering (Kumar et al., 2005), wet chemical etching (Böttler et al., 2012), as well as electrochemical etching (Pust et al., 2011). Details of these techniques will be discussed in the next chapter.

The reasons behind high popularity of ZnO patterning are due to the enhancement in certain optical characteristics especially on the photoluminescence characterization which allows it to be applied into various applications mentioned in the earlier paragraph. Besides that, research found that by fabricating patterned ZnO, higher surface to volume ratio (Ching et al., 2013c)could be obtained as compared to conventional thin films. By applying this into devices such as sensors or light emitting device, it is believed that the performance of the devices will be greatly increased (Wang et al., 2007b).

Till today, a lot of researches have been carried out by groups of researchers to study the fabrication methods of surface patterning of ZnO. Some of the methods that are widely used are mentioned in the earlier paragraphs. Details for these fabrication methods will be further discussed in the literature review chapter. Throughout the literature studies, we found that electrochemical etching of ZnO thin films is still at a very young development age. Limited studies have been carried which reflects the immaturity of this fabrication technique and there are still a lot of areas that could be explored in order to optimize the potential of this fabrication technique.

To contribute to the understanding of porous ZnO thin films fabrication via electrochemical etching, systematic studies on this fabrication method as well as the structural and optical characterizations of its products have been carried out in details.

1.2 Research objectives

The main objectives of this study are:

- To fabricate porous ZnO thin films via electrochemical etching method.
  - The effects of etchant concentrations, etching potentials and etching time on the fabrication of porous ZnO thin films are carried out systematically.
- To study the optical and structural properties of porous ZnO thin films via scanning electron microscope (SEM), photoluminescence (PL) spectroscopy and Fourier transform infrared (FTIR) spectroscopy.
- To determination the porosity and thicknesses of porous ZnO thin films via infrared (IR) reflectance spectra with the use of effective medium theories.

1.3 Research originality

Throughout literature studies, it is noticed that current trends in ZnO nanostructure and porous fabrication concentrate on the bottom-up growth. It is known that the electrochemical etching method had been developed and utilized for many years. Majority of these studies are carried out on other materials such as gallium nitride (GaN), aluminum oxide (Al_2O_3), silicon carbide (SiC). The utilization of the top-down fabrication methods, especially the electrochemical etching of ZnO, has not been receiving as intense attention as the materials aforementioned. Till today, there are only several studies had been carried out to fabricate patterned surface ZnO thin films via electrochemical etching. Thus, systematic studies on the fabrication of porous ZnO, i.e., the focus will be given to the optimization of etching parameters, surface morphological and cross sectional characterization as well as their optical properties. Besides that, infrared (IR) reflectance studies on the porous ZnO have also been carried out in this study. Up to date, there are yet any work has been reported on the IR reflectance characteristic of porous ZnO with the use of effective medium theories and standard multilayer optic technique. Do note that, in this study, the IR reflectance study will be concentrating on the demonstration of retrieving the porosities and thicknesses of the porous ZnO thin films with the use of homebuilt fitting software, where effective medium theories and standard multilayer techniques have been incorporated into the software. However, the effective theories used for the fitting will be briefly discussed and introduced in Chapter 5.

Apart from that, the observation in the SEM study has also led to a relatively new finding where porous ZnO thin films with different voids concentration at different depth in the thin films has been obtained. This finding was applied in the assumption during the IR reflectance spectra fitting and the results showed that both experimental and fitting curves were in well agreement with one another. Thus, the SEM results validate the assumption used in the IR fitting.

1.4 Scope of study

In this research study, undoped ZnO thin films deposited on n-type silicon (Si) substrates with (111) preferred orientation by radio frequency (RF) sputtering technique was used. The deposited wafers (2 inch wafer) were cut into smaller pieces with dimension of 10 mm × 10 mm. The samples were electrochemically etched with the use of potassium hydroxide (KOH) etchant in a home fabricated Teflon etching cell. In this study, two electrodes cell system was used. Platinum rod was used as the counter electrode while ZnO thin films deposited on Si substrates were the working electrode. During electrochemical etching process, the etching cell was supplied with a direct current potential from a power supply. Besides that, fixed powered ultraviolet (UV) light was illuminated on the experiment setup to enhance the electrochemical etching process.

The fabrication of porous ZnO thin films in this study were divided into three parts which separately studied the effects of etchant concentrations, etching potentials and etching time on the fabrication of porous ZnO thin films. In each of the experiments, only one of the parameters was varied while the other parameters will be fixed. The justification of the fixed parameter chosen was based on certain criteria which will be clearly stated in future chapters. This was to ensure that the results of the experiment were not interfered by other factors that were induced by variation of other parameters. The samples obtained from the experiments were characterized by SEM, PL spectroscopy and FTIR spectroscopy to obtain their optical properties, surface morphologies and cross sectional structures. Finally, the determination of porous thin films thicknesses and porosities for selected samples were determined with the use of fitting technique.

1.5 Organization of dissertation

This dissertation is divided into six chapters to elaborate the content of this work in detail. After a brief introduction in this chapter, the literature study will be discussed in Chapter 2. After that, fundamental physical and optical properties of ZnO, the introduction to the RF magnetron sputtering technique as well as the electrochemical etching of ZnO thin films will be presented in detail in Chapter 3.Besides that, the working principle of the characterization instruments will be discussed in brief. In Chapter 4, detailed discussions about material and samples preparation as well as the parameters used for characterizations are carried out. In Chapter 5, the characterization of the samples for each set of experiments is presented and discussed. Note that there are three experiments carried out which separately studied the effects of KOH concentrations, etching potentials and etching time to the electrochemical etching of ZnO thin films. The samples obtained from each experiment are characterized by means of SEM, PL spectroscopy and FTIR spectroscopy. The results of the characterizations for samples from each set of experiments will be discussed in Chapter 5. At the end of this chapter, results from the IR reflectance spectra fitting are discussed. Finally, Chapter 6 contains the summary of the entire work and some brief discussion on the potential direction for future research study on fabrication of the porous ZnO thin films.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter briefly discusses the development of ZnO surface patterning techniques. The discussion on the literature review will begin with an overview of the bottom-up growth methods of surface patterning methods. Then, the etching methods used for pattern surface material fabrication will be discussed later.

2.2 Overview of ZnO surface patterning methods via bottom-up growth methods

Since year 2000, ZnO has entered a new era in material science as it receives substantial interest in surface patterning research studies. As mentioned in the earlier chapter, the current development on ZnO surface patterning concentrates more on the bottom-up growth methods. Various methods have been employed in order to obtain desired patterned or modified surface ZnO. The bottom up growth method is the deposition method that grows the patterned structure from the substrate/seed layer surface up to certain desired thicknesses. These fabrication methods can be categorized into several types, such as chemical vapor deposition (CVD), electrochemical deposition, sol gel methods and hydrothermal growth. In this chapter, we will discuss each of the above mentioned methods in detail together with a brief discussion on the characterization results of the samples. Before intense discussion is carried out, it is good to understand the definition of porous and porosity. A porous material is a material which contains voids or also known as pores within it. In many cases, etched pits type porous structure is observed where the porous material contain many small surrounded by the solid material itself to form a sponge like structure. In some cases, especially in this study, the porous material can also exist in the form, where the grains of solid materials are surrounded by air voids to form the hillock like porous structure. In order to enable the porous structure to be defined as nanoporous, the size of the pore in the pits like porous structure has to be as small as 100 nm or below with high density of pores distributed in the material. For hillock like porous structure, the size of the grains surrounded by the voids is also need to be smaller than 100 nm. Otherwise, the material will be named as microporous or macroporous material. On the other hand, the terms of porosity is defined as the volume fraction of voids contained in a material. In other words, the porosity can be the ratio of the voids volume over the total volume of the material. The porosity is often presented in the unit of percentage to measure the amount of voids in the porous materials.

2.2.1 Chemical vapor deposition

CVD is a deposition technique of solid thin films to a surface of substances or substrates which involves a chemical reaction of vapor phase precursors (Jones and Hitchman, 2009). There are many types of CVD deposition techniques have been developed, such as thermal CVD, laser pulsed CVD, plasma enhanced CVD and other variant CVD. The choice of CVD techniques that was employed depends on many factors such as materials' requirements, research preferences and other factors. In the paragraphs below, several examples of the deposition of ZnO nanostructure via several CVD techniques will be discussed briefly.

Li et al. (2012) reported the fabrication of nanoporous ZnO thin films with the use of CVD technique. This study employed the mixture of ZnO and hydrochloric acid (HCl) to form zinc chloride, as precursor. The ZnO thin films were deposited on sapphire (Al_2O_3) inside the furnace at a growth temperature of 850 °C/ min. The results of the structural characterization revealed that a uniform nanoporous ZnO thin film with quasi nanoporous is obtained as shown in Fig. 2.1. The size of the

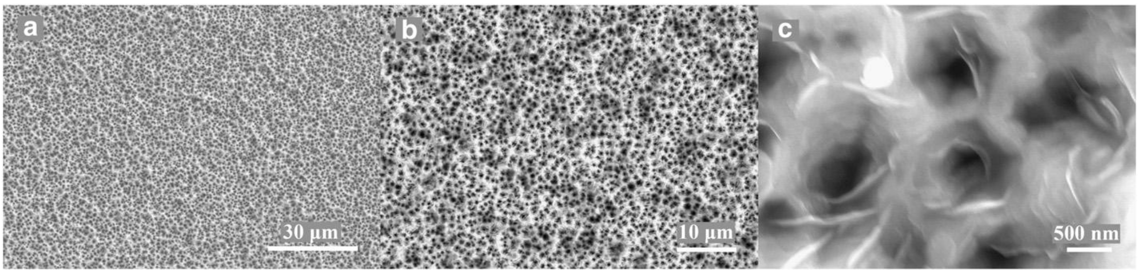


Fig. 2.1 Nanoporous ZnO obtained from CVD technique (Adapted from Li et al., (2012).

pores are about 500 nm as estimated from SEM images. Besides that, the XRD results also show that high crystalline quality wurtzite nanoporous ZnO thin films were obtained through this technique as intense ZnO(002) peak was observed. Besides peaks that were originated from ZnO(002), ZnO(004), and Al_2O_3, no other peak is observed in the XRD spectra, which means highly *c*-oriented nanoporous ZnO thin films are obtained.

Cheng et al. (2008) introduced thermal CVD method of ZnO for dye-sensitized solar cell fabrication. It is believed that this method possesses a lot of advantages such as achievable of high crystallinity, capability to produce various surface morphology as well as less chemical contamination. In this work, ZnO nanostructure was deposited on the indium tin oxide (ITO) coated glass substrates via liquid nickel catalyst assisted double source double tube thermal CVD. The ZnO nanostructure was deposited in the argon (Ar) and oxygen (O_2) gas mixture while zinc (Zn) powder was used as precursor. The deposition process was carried out at a temperature of 500 ℃. The SEM characterization of this work revealed that ZnO nanorods were successfully obtained. The average diameter of the nanorods was about 70-100 nm while the XRD spectra showed that ZnO(002) dominated ZnO was deposited. However, the observation of ZnO peaks that were originated from other phase showed that multiple phase originated ZnO was obtained.

Apart from the two examples discussed in the above paragraphs, Chang et al. (2004) also introduced another new variant of CVD technique to fabricate patterned ZnO nanostructure. In this study, the authors employed a technique called vapor trapping CVD methods. In this technique, vapor trapping design was incorporated into the CVD system by inserting a quartz vial into the quartz tube with 3 chips placed outside and inside the vial. The schematic diagram of the experimental setup is presented in Fig. 2.2. One of the chips which contained pure Zn powder was placed in the vial to create Zn rich ambient in the vial. It is believed that this vapor trapping design in the CVD is able to facilitate and control the carrier concentration. During the deposition process, the quartz tube in the CVD system was in an Ar gas ambient with 700 °C under a constant flow of Ar gas at 90 sccm. After that, a mixture gas of 2% O_2 and 98% Ar was flown into the quartz tube for 30 min. The SEM images in this study revealed that different kinds of ZnO nanostructures (nanorods, nanowire, nanocombs and nanoneedles) were observed at different spots on the samples. The deposition of different nanostructures in the sample was due to different Zn and O_2 vapor concentration at each spot.

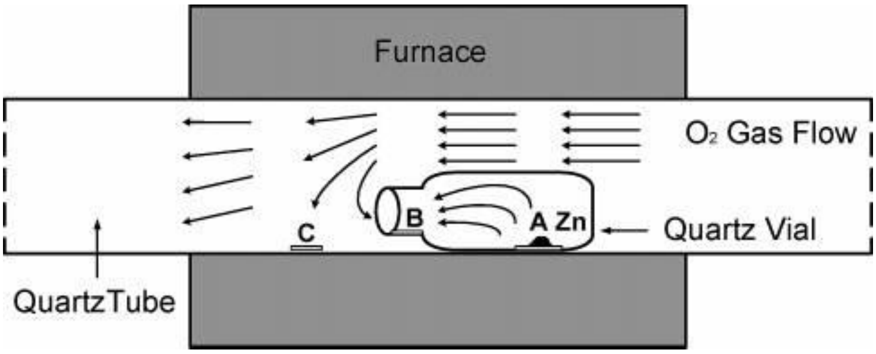


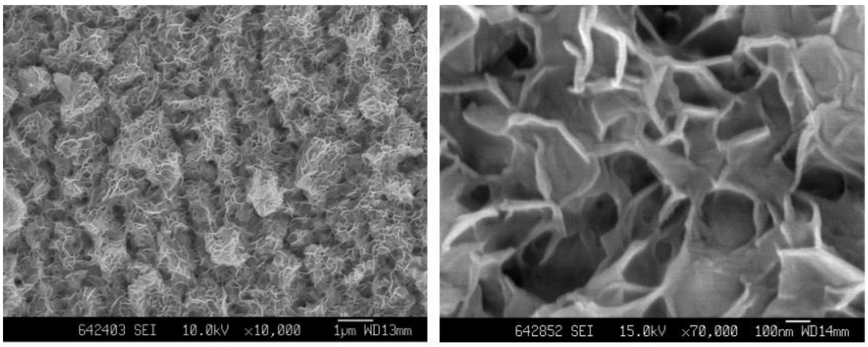
Fig. 2.2 Schematic diagram of the experimental setup of vapor trapping CVD (Adapted from Chang et al., 2004).

Note that the work discussed above is only a small part of the research work reported. There are more studies reported which involve the use of conventional and modified CVD techniques. Through literature study, it is learnt that various types of ZnO nanostructures can be fabricated with diverse experimental setup. This has made CVD become one of the common methods in obtaining porous and nano structured ZnO. Nonetheless, the CVD fabrication method requires relatively bigger efforts in optimizing the etching parameters as there are several key parameters such as temperature, gas flow as well as the use of suitable catalyst that require precise tuning in order to obtain a good nanostructure.

2.2.2 Electrochemical deposition

Electrochemical deposition is another type of bottom up deposition method which is frequently used for deposition of ZnO nanostructure as well as porous ZnO. This method uses the principle of electrochemistry to attract the targeted ions towards the substrates. By applying a negative bias on the substrates, zinc ions (Zn^{2+}) will be attracted to the substrates. On the substrates surface, Zn^{2+} will react with the hydroxide ions (OH^-) to form ZnO molecules and attach on the substrate. Continuous repetition of this process will allow increasing layer on the substrates.

There have been many studies reported on the success in depositing ZnO thin films with various types of structure. Li et al. (2007) demonstrated the success in depositing nanoporous ZnO thin films on copper (Cu) substrates by electrochemical deposition method. In this work, a simple three electrode cell was used whereby 99.99% of platinum (Pt) was used as the working electrode in cyclic voltammogram while in the electrochemical deposition, the reference electrode, auxiliary electrode and working electrode used were graphite rod, saturated calomel electrode and pure Cu foil, respectively. During the deposition process, Zinc chloride ($ZnCl_2$) solution was used as the electrolyte and the source of Zn^{2+} ions. The deposition was carried out with the application of current density in the range of 0.01 to 1.00 mA/cm^2 under the temperature between70-90 °C. The SEM characterization of this study showed that nanoporous ZnO which composed of random growth of nanosheet was obtained in the sample surface (as shown in Fig. 2.3). The thickness of the nanosheet was about 10 to 20 nm. Besides that, the XRD studies confirmed that success of depositing wurtzite ZnO thin films on the Cu surface where the peaks in XRD spectra are originated from wurtzite crystal structure of ZnO.



(a) (b)

Fig. 2.3 ZnO nanosheet obatained from electrochemical deposition (Adapted from Li et al., 2007).

Besides that, many reports (Azaceta et al., 2009; Kim et al., 2010) have shown that ZnO nanostructures could be obtained through electrochemical deposition techniques. The diverse requirement in ZnO based devices development and creativity among the research community have brought advancement in electrochemical deposition technique. Today, the fabrication of well ordered honeycomb like ZnO porous structure has become possible. Liu et al. (2005) demonstrated the success on depositing well ordered honeycomb like porous ZnO by using electrochemical deposition. In this study, the authors deposited the ZnO thin films on the polystyrene spheres (PS) covered ITO glass substrates with the use of a potentiostat. A standard three electrode cell was connected to the potentiostat to initiate the deposition process. Upon the deposition process, the substrate was placed in a thermo regulated bath of zinc nitrate ($Zn(NO_3)_2$) solution with the temperature varies from 50 to 90 °C and a potential of 1.1 V was applied throughout the deposition process. After the deposition process, the organic substance was removed by dipping the sample in toluene for 24 hours. The characterization results showed

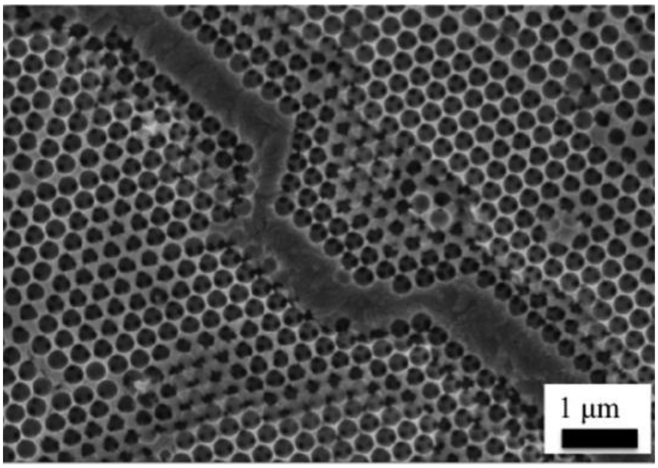


Fig. 2.4 Well-ordered honeycomb like porous ZnO obtained from electrochemical deposition of ZnO on PS covered ITO glass substrates (Adapted from Liu et al., 2005).

that well ordered honeycomb like macroporous structure had been obtained. Besides that, the characterization results also showed that polycrystalline ZnO with strong (002) preferential orientation was obtained. The study also reported that electrolyte concentration had direct effect on the growth rate where higher concentration of electrolyte will lead to higher deposition rate.

Additionally, Xu et al. (2006) also demonstrated the deposition of periodic array ZnO via electrochemical deposition technique. In this study, a layer of photoresister was coated on the substrates and photolitographed to create an array template for deposition. The electrochemical bath process took place in a glass cell water bath under a temperature of 65 ℃. An argentum (Ag) electrode was used as the reference electrode while a 99.99% purity zinc plate was connected to the anode of a potentiostat, while the cathode of the potentiostat was connected to the patterned substrate. A solution that contained $Zn(NO_3)_2$ with 6.0 pH value was employed as electrolyte. The SEM images of the sample showed that rod patterned periodic array of ZnO was successfully deposited. The diameter of each rod as observed from cross sectional view was about 500 nm to 1 μm. The measured XRD patterned revealed that wurtzite ZnO(002) dominated thin film was obtained.

From the literature studies, it is understood that various types of patterned ZnO surfaces can be deposited via electrochemical deposition. Besides that, well aligned array of patterned ZnO can be deposited with the assistance of various types of templates such as photolithographed templates as well as PS covered substrates. There are more works reported on the success of the electrochemical deposition method in ZnO thin films. As this method is not the main research objective of this research study, only a few works is included for introductory purpose.

2.2.3 Hydrothermal method

Hydrothermal method is another synthesis method that is widely used for ZnO fabrication. It is a method that requires high ambient temperature and pressure to crystallize material during the fabrication (Byrapa and Masahiro, 2001). The hydrothermal method was initially being widely used for single crystal material synthesis. This method was developed for the geological studies and it was later being adopted for the fabrication of quartz single crystal. Today, hydrothermal has gone through a revolution in producing new product which is the patterned surface materials. This method has been studied by many researchers to produce several types of patterned materials, especially on ZnO material system.

Through literature study, it is noticed that the growth of patterned surface ZnO via hydrothermal method was initiated around the year of 2000. The initiation of patterned surface ZnO fabrication by using hydrothermal method began around the year of 2005 where the outcomes of this fabrication method were reported after the year of 2005. Lu and Yeh (2000) was among the earliest research groups to report the fabrication of ZnO microstructure through hydrothermal technique. However, the output of this particular study was in powder form instead of thin films that have been intensely discussed in the earlier section. In the study by Lu and Yeh (2000), the ZnO nanostructure powder was synthesized through hydrothermal method with the use of ammonia as alkaline source. The effects of the reaction temperature and time toward the changes on the microstructure and particle size were studied. To synthesize nanostructure ZnO, $Zn(NO_3)_2$ was diluted into deionized water to prepare cation solution. Ammonia was added into the $Zn(NO_3)_2$ solution to precipitate the Zn cation. The precipitates were introduced into the autoclave apparatus and deionized water was added. During the reaction, the temperature and time were set in the range of 100 to 200 ℃ and between 0.5 to 2 hours, respectively.

The SEM images revealed that ellipsoidal shape of ZnO particles were obtained. The study showed that ZnO particles were rapidly formed when temperature reached 100 ℃ while the prolonged time did not change the nanostructure much. The increase of the temperature slightly reduced the particle size while it was known the characteristics of ZnO particles depended on the pH level of the starting solution. The XRD pattern also revealed that hexagonal structured ZnO has been synthesized through hydrothermal method.

Numerous studies have also revealed that the synthesis of porous ZnO in microrods is also possible with the use of hydrothermal technique. Jeon et al (2010) demonstrated the synthesis of ZnO nanorods with porous structure distributed on each of the rods. This study started with the deposition of seed layer via spin coating methods. The solution which consisted of zinc acetate in 2-methoxyethanol as a solvent, and monoethanolamine was used as the solution for the seed layer. After that, the hydrothermal growth of ZnO was initialized by immersing the substrates with the seed layer in an aqueous solution of zinc nitrate hexahydrate [$Zn(NO_3)_2$ 6H2O] and hexamethylenetetramine (HMT) inside an autoclave under the temperature of 140 ℃ for 6 hours. After the hydrothermal process, the samples were annealed in 3 different temperatures to visualize the effects of the annealing temperature on the samples.

From the SEM images, it could be seen that hexagonal microrods with nanoporous structure were obtained through the synthesis process. It was also noticed that the ZnO microrods had grown vertically on the substrates with uniform length distribution. Besides that, XRD spectra also confirmed that the samples were in wurtzite crystal structure as only reflection peaks from ZnO(002) and ZnO(004) were observed. On the other hand, the pore density and pore diameter analysis revealed that pore density increased over the increase of temperature and pore diameter was decreased as annealing temperature decreased.

Apart from that, literature studies of the synthesis of ZnO via hydrothermal technique show the ability of this technique to synthesize diverse shape of ZnO nanostructure. One of the most recent studies by Xu et al. (2012) reported the synthesis of comb like ZnO nanostructure by using one step hydrothermal synthesis. The ZnO nanostructures were grown on Si substrate. Prior to hydrothermal growth, $Zn(NO_3)_2$ 6H2O was mixed with HMT at room temperature which would then be used as growth solution while gold (Au) nanowire catalyst was dispersed on the substrate uniformly. The Si substrate with Au nanowire was loaded inside the Teflon holder which contained the well mixed growth solution. The hydrothermal growth was initiated with the temperature of 90 ℃ for 16 hours.

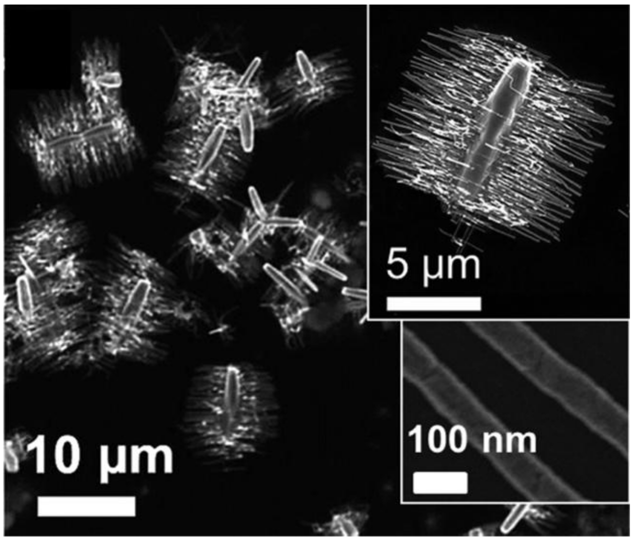


Fig. 2.5 Comb-like ZnO nanostructure obtained by Xu et al. (2012).

Through surface morphology studies, it was observed that the ZnO nanostructures were found throughout the substrate. Comb-like nanostructures with stem in the middle and branches at both sides of the stem were observed (as shown in

Fig. 2.5). It was known that the ZnO nanostructure could be controlled by the reaction kinetics reactant concentration and time. Through the time dependent growth studies, it was found that the stems reached a constant value of length after 6 hours of growth while the length of the branches reached a constant value at 12 hours.

It is learnt that hydrothermal synthesis methods capable to grow various types of nanostructure and porous ZnO instead of the conventional growth ZnO single crystal or any other crystal growths which have been widely used decades ago. However, it also noticed that hydrothermal growth considered as complex synthesis technique as it requires extra care on the safety measures as the growth processes is conducted under high temperature and pressure. Besides that, the combination of correct growth parameters is also found to be crucial to enable the growth of good quality samples.

2.3 An overview of patterned ZnO via etching methods

The fabrication of patterned surface or modified surface ZnO via bottom-up growth methods has been extensively studied in the earlier subchapter. Besides the bottom-up fabrication methods, there is another category of method in fabricating porous and nanostructure of ZnO which is known as etching method. There are basically three subcategories in the etching method, namely, electroless etching, electrochemical etching and dry etching. The first two categories require the use of chemical as an etching medium while the third one normally employs the plasma to initiate the etching process. As dry etching is not commonly used for nanostructure and porous fabrication, the details and literature study of this method will not be included in this subchapter.

2.3.1 Electroless etching

Electroless etching is one of the top-down fabrication methods that has been used for fabrication of porous and patterned surface material. This method employs the corrosive nature of its etchant to react with material surface to obtain porous structured as well as other patterned surfaces. It has commonly been used to fabricate porous structured and patterned surface for material such as Si (Kolasinski and Gogola, 2012), silicon carbide (SiC) (Rittenhouse et al., 2003), gallium nitride (GaN) (Nie et al., 2012) and etc. For ZnO material system, it is found that this method has been used in the etching of the bulk ZnO material. Many studies have been conducted to understand the etching behavior of ZnO (Mehta and Meier, 2011; Petukhov et al., 2007) as well as the micro patterning (Takahashi et al., 2005) of bulk ZnO with the aid of patterned mask. Apart from that, our research group had also recently published an article about the electroless etching of ZnO thin films that was deposited on the Si substrates by RF magnetron sputtering (Ang et al., 2012). In the following paragraphs, a few studies on the electroless etching of ZnO material system will be briefly discussed.

Sun et al. (2007) ago has shown the realization of controllable etching of ZnO films via wet chemical etching. In this study, ZnO thin films were initially deposited on the sapphire substrate via pulsed laser deposition (PLD) technique. The deposited thin films were later treated with various concentration of ammonium chloride (NH_4Cl). The relation between the etching time with etching thickness was also studied by a selected concentration of 5% NH_4Cl. From the profilometer scanning measurement, it was shown that the etching rate had nearly linear relationship with etchant concentration where this near linear relationship has been related to the increase of oxonium ions with the increase of the NH_4Cl concentration. Besides that, the etching time dependent study carried out by Sun et al. (2007) also revealed that the root mean square surface roughness of ZnO thin films increased over etching time. Simultaneously, the grain sizes were decreased as the etching time increased. The results have apparently led to a conclusion that controllable etching of ZnO could be achieved.

Böttler et al. (2012) have reported the electroless etching of ZnO thin films. The study basically employed RF magnetron sputtering method to deposit various thicknesses of ZnO thin films on the glass substrates. After that, the thin films were etched with electroless etching methods with the use of HCl solution at various etching time to obtain the textured surface. The characterization results showed that crater like on ZnO surfaces were obtained after the etching. Atomic force microscopy (AFM) also revealed that for a given thickness, the crater dimension was increased over etching time while statistical analysis showed that the surface roughness initially increased sharply before it got into saturation as the etching time was further increased. The sharp increment of roughness was related to the etching rate in vertical and lateral direction which suggested non-uniformity in ZnO layer with respect to etching where fast initial etching occurs along grain boundaries and area with low compactness. It is also known that different structures had been developed through etching when different initial thicknesses of the ZnO thin films were used. The variation of the craters depths has significantly varied as compared to the craters' diameter and led to the synthesis of various types surfaces through the etching process. The obtained textured surfaces were later applied for the studies in solar cell applications.

2.3.2 Electrochemical etching

The electrochemical etching method was a method that utilizes the principle of electrochemistry where both chemical (etching medium) and external potential application are involved in the etching process. The chemical used is varied depending on the material intended for etching whereby it is normally an acidic or alkaline solution. While the application of potential will produce space charge effect in the thin films which enhance the etching process. Electrochemical etching has become a common treatment or surface patterning method in many material systems such as Si (Navarro et al., 1999; Um et al., 2011), alumina (Al_2O_3) (Rabin et al., 2003), SiC (Shishkin et al., 2004), GaN (Yam et al., 2007; Al-Heuseen et al., 2011; Cheah et al., 2013), where many studies have been carried out to understand the etching behavior as well as to carry out surface patterning for various applications. However, through literature study, it is found that electrochemical etching on ZnO material system is still in its infancy stage and has not been fully explored. There are only limited numbers of work or publications could be found throughout the research community that is related to the electrochemical etching of ZnO. This is one of the reasons why the electrochemical etching method is chosen in this study.

The work carried out by Basu et al. (2008) is one of the earliest work that is related to the formation of porous ZnO via electrochemical etching method. However, the formation of porous ZnO was conducted by the electrochemical etching of pure Zn. The author utilized the corrosive and oxidizing nature of electrochemical etching to form the porous ZnO. In this work, high purity Zn was electrochemically etched with the use of several concentrations of oxalic acid with the application of constant voltage of 10V. During the etching process, the Zn was connected to the anode of power supply while the cathode was connected to a Pt rod. The experiment was carried out with and without the presence of UV light to understand the effects of the presence of UV light as compared to the samples from dark electrochemical etching.

The XRD characterization of the samples showed that polycrystalline ZnO had been obtained from the experiment. It was also noticed that the intensity of ZnO XRD peaks increased with the presence of UV light for every concentration of etchant used. The authors believed that the increase of the ZnO XRD peaks intensity was attributed to the crystal growth of ZnO which was caused by enhanced rate of oxidation. The enhancement of oxidation rates were due to holes generation in Zn. The field emission scanning electron microscopy (FESEM) study of nanoporous ZnO showed that pore diameter increased with the presence of UV light. The author claimed that the existence of UV light has further influence the high grain growth of ZnO. Thus the existence of UV light played an important in the formation of ZnO in the study.

Pust et al. (2006) has performed the electrochemical etching of aluminum (Al) doped ZnO thin films for solar cell application. The ZnO thin films were deposited by using RF-sputtering technique with the thickness of 800 nm. The electrochemical etching of the ZnO thin films were carried out with the use of three-electrode setup assisted by a potentiostat under a constant temperature of 25 ℃. HCl and potassium sulfate solution were employed as the etchant solution for the electrochemical etching process.

The SEM characterization revealed that both type of etchant produced similar type of surfaces which was crater like ZnO surface (as shown in Figs. 2.6). This led to a conclusion by the authors claiming that the composition of the electrolyte did not influence the surface morphology significantly in the electrochemical etching process. As long as the solutions were kept at neutral range, they would produce similar type of surface morphologies. However, as the etching time increased, gradual changes of the surface morphologies of the samples were observed.

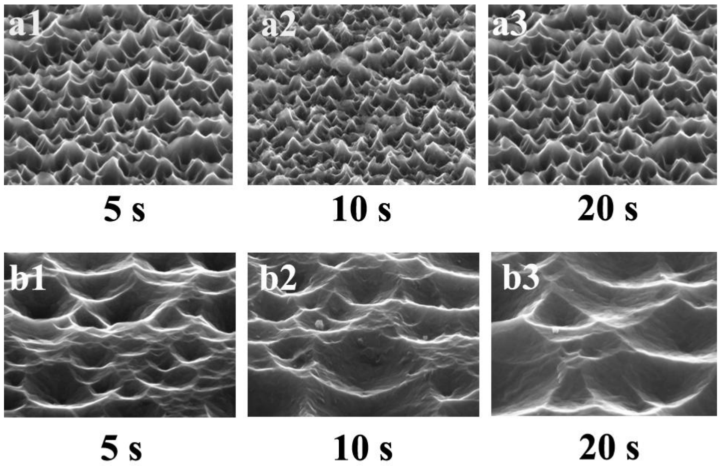


Fig. 2.6 Surface morphologies of ZnO surface etched with a) potassium sulfate b) HCl (Adapted from Pust et al., 2006).

Klemm et al. (2012) also demonstrated similar study as Pust et al. However, the electrochemical etching of Al doped ZnO thin films were aimed for photovoltaic applications. In the study, the ZnO thin films were prepared by depositing the thin films on glass substrates via RF-magnetron sputtering technique. The thicknesses of the sputtered thin films were approximately 800 nm while the etchant used in this study was a mixture of sodium acetate, HCl, and sodium chloride (NaCl) in several pH values. Note that the experiment was carried out in a three electrode cells system with the use of a potentiostat. The experiment revealed that, grooved surface was obtained through electrochemical etching of ZnO thin films (as shown in Fig. 2.7). The authors also claimed that that was influenced by grain boundaries that initially formed on the as grown samples. It was also known that the etching of the ZnO thin films at near neutral pH value was diffusion controlled as Zn dissolution rate increased with the concentration of H^+ ions. This study also showed that electrochemical etching procedure dissolved the ZnO from the grain boundary which was caused by lattice decomposition and local pH shifts. Furthermore, this study also shows that the changes of pH value resulted changes in the samples surface morphology. This is owed to the Zn dissolution rate increase linearly with the H^+ and acetate buffer concentration.

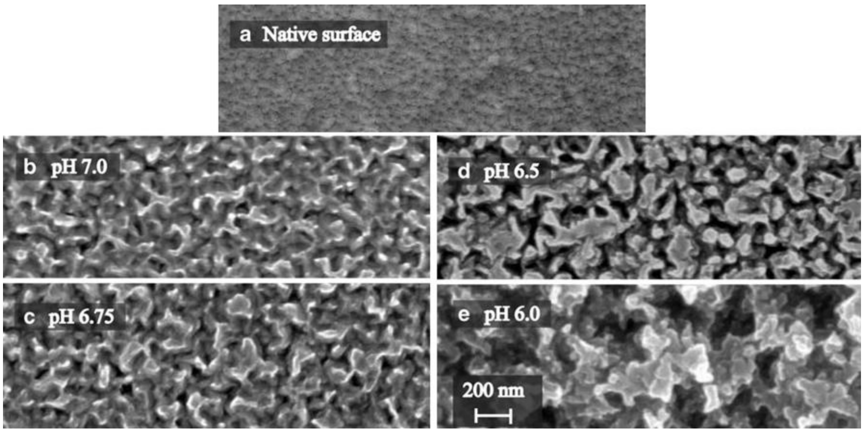


Fig. 2.7 Grooved ZnO surface obtained from electrochemical etching of ZnO (Adapted from Klemm et al., 2012).

The electrochemical etching is one of the versatile methods in producing patterned surface especially on the porous media fabrication. It requires less controllable parameter which allows high percentage of repeatability. Additionally, the investigation of electrochemical etching on ZnO material still remains at initial stage as very limited studies have been carried out and reported. Thus, the electrochemical etching of ZnO poses high potential in producing patterned surface ZnO which is yet to be discovered.

2.4 Optical properties of patterned surface ZnO

Optical properties of patterned surface have always been an important studying subject due to the necessity of understanding its optical properties for applying it into relevant devices as well as solar cell applications. PL studies have been gaining an intense interest among researchers who study ZnO micro and nanostructure as well as porous ZnO. This is due to the ability of this characterization to reveal the changes in bandgap energy, surface to volume ratio as well as the occurrence of point defects in the thin films. Besides that, the characterization with the use of FTIR spectroscopy is also an interesting subject to study. To the best of our knowledge, there are yet any specific study has been conducted to thoroughly investigate the IR response of the patterned surface ZnO. In the following paragraphs, a brief introduction will be discussed on the optical properties of the patterned surface ZnO in term of PL and FTIR characterization.

PL characterizations have been playing an important role in the fabrication and characterization of porous media. For ZnO porous and nanostructure, many research studies (Lin et al., 2010; Sun et al., 2007)have opted this characterization for many reasons. One of the reasons is the enhancement of PL emission intensity of the patterned surface ZnO. Through the literature study, the enhancement of PL intensity is normally observed on the ZnO porous and nanostructure. This is due to the increment of the surface to volume ratio (Phan et al., 2010; Erki et al., 2011) of the ZnO thin films. The amplification of the PL emission intensity is ascribed as the result of a stronger extraction of the light scattering from side wall of the nanostructure and porous ZnO as the surface to volume ratio increases.

Another reason why PL is important in patterned surface ZnO characterization is due to the ability of this characterization to detect point defects