



**FABRICATION AND CHARACTERIZATION OF ZnO
NANOSTRUCTURES FOR DNA DETECTION**

by

FOO KAI LOONG
0941710372

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LIST OF ABBREVIATIONS

AFM	Atomic force microscope
2-ME	2-methoxyethanol
Ag/AgCl	Silver/silver chloride
APCVD	Atmospheric pressure chemical vapor deposition
APTES	(3-Aminopropyl)triethoxysilane
BioFET	Biomolecular field effect transistor
BOE	Buffer oxides etch
CHEMFET	Chemical field-effect transistor
CHIT	Chitosan
CNTs	Carbon nanotubes
CO	Carbon monoxide
CO ₂	Carbon dioxide
C-V	Cyclic voltammetry
CVD	Chemical vapor deposition
DC	Direct current
DEA	Diethanolamine
DEZ	Diethylzinc
DIW	Deionized water
DNA	Deoxyribonucleic acid
DNAFET	DNA field effect transistor
DPV	Differential pulse voltammetry
dsDNA	Double-strain DNA
EDX	Energy-dispersive X-ray
EnFET	Enzyme field-effect transistor
EtOH	Ethanol

FESEM	Field emission scanning electron microscope
FET	Field effect transistor
FTIR	Fourier transform infrared spectroscopy
FWHM	Full-width at half-maximum
GCE	Glassy carbon electrode
GNPs	Gold nanoparticles
HMT	Hexamethylenetetramine
IDE	Interdigitated electrode
IDT	Interdigitated transducers
IEP	Isoelectric point
In ₂ O ₃	Indium oxide
IPA	Isopropyl alcohol
ISFET	Ion-sensitive field-effect transistor
ITO	Indium tin oxide
IUPAC	International Union of Pure and Applied Chemistry
JFET	Junction field-effect transistor
LiNbO ₃	Lithium niobate
LPCVD	Low-pressure chemical vapor deposition
MEA	Monoethanolamine
MEMS	Microelectromechanical system
MeOH	Methanol
MOCVD	Metal-organic chemical vapor deposition
MOSFET	Metal-oxide-semiconductor field-effect transistor
MWNTs	Multi-walled carbon nanotubes
NaOH	Sodium hydroxide
NRs	Nanorods
NWs	Nanowires

O ₂	Oxygen gas
PBS	Phosphate buffer saline
PCR	Polymerase chain reaction
PECVD	Plasma-Enhanced chemical vapor deposition
PL	Photoluminescence
PVD	Physical vapor deposition
RF	Radio frequency
RMS	Root-mean-square
RT	Room temperature
SAW	Surface Acoustic Wave
SCE	Saturated calomel electrode
SiCl ₄	Silicon tetrachloride
SiI ₂	Silicon diiodide
SiO ₂	Silicon dioxide
SPR	Surface plasmon resonance
ssDNA	Single-strain DNA
T	Transmittance
TEA	Triethanolamine
TiO ₂	Titanium oxide
T-RFLP	Terminal-restriction fragment length polymorphism
UV	Ultraviolet
UV-Vis-NIR	Ultraviolet-visible-near infrared
VLS	Vapor-liquid-solid
V-S	Vapor-solid
XRD	X-ray diffraction

LIST OF SYMBOLS

Ag	Silver
Al	Aluminium
Ar	Argon
Au	Aurum
C	Carbon
Cd	Cadmium
Cu	Copper
E_g	Energy band gap
ϵ_∞	Optical dielectric constant
F	Farad
Fe	Iron
$h\nu$	Photon energy
Hz	Hertz
In	Indium
Mg	Magnesium
mg	milligrams
mm	millimeter
Mo	Molybdenum
n	Refractive index
Ni	Nickel
nm	nanometer
O	Oxide
rpm	rounds per minute
Se	Selenium

Z	Impedance
Zn	Zinc
α	Absorption coefficient
$\alpha h\nu$	Optical band gap
λ	Absorption band edge
Ω	Ohm
$^{\circ}\text{C}$	Degree Celsius
μm	micrometer
\AA	Angstrom

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Fabrikasi dan Sifat-sifat Struktur Nano ZnO Untuk Pengesanan DNA

ABSTRAK

Zink oksida (ZnO), wakil kumpulan II-IV logam-oksida bahan semikonduktor kini dikaji secara meluas di kalangan penyelidik. ZnO dengan jurang jalur yang lebar (3,37eV) dan loncatan tenaga ikatan yang besar (60 meV) memberi kelebihan sifat-sifat dalam elektrik dan optik. Oleh kerana sifat-sifat yang unik dan kesenangan untuk pertumbuhan dengan menggunakan kaedah bawah-ke-atas bergabung dengan titik isoelektrik yang tinggi, bebas dari toksik, nisbah luas permukaan dengan isipadu yang besar, selamat dan sesuai untuk biomolekul, struktur nano ZnO mempunyai minat yang besar dalam aplikasi pengesanan biologi. Tujuan penyelidikan ini adalah untuk sintesis, fabrikasi, dan mengkaji sifat-sifat sensor berasaskan struktur nano ZnO untuk mengesan penetapan dan penghibridan DNA. Two jenis struktur nano ZnO telah dikaji, iaitu filem nipis dan rod nano. Ketelusan ZnO filem nipis yang baik telah berjaya disintesis dengan menggunakan kaedah sol-gel penyalutan dengan cara putaran yang mudah caranya dan rendah kosnya. Rod ZnO dengan skala nano yang memiliki struktur kristal yang tinggi kemudian ditumbuhkan atas filem nipis yang disediakan dengan menggunakan cara pertumbuhan hidroterma pada suhu rendah. Dalam tesis ini, kami mengkaji pengaruh pelarut yang berbeza pada struktur, optik dan sifat elektrik struktur nano ZnO. Empat jenis pelarut iaitu metanol, etanol, isopropanol, dan 2-methoxyethanol telah dipilih untuk penyediaan larutan benih ZnO. Keputusan yang diperhatikan dengan menggunakan FESEM menunjukkan partikel nano dan rod nano dengan saiz masing-masing kurang daripada 40 nanometer dan 60 nanometer telah berjaya disintesis. Peninjauan ke atas sifat optik dengan menggunakan UV-Vis-NIR spektrofotometer mengesahkan bahawa ZnO diklasifikasikan sebagai bahan semikonduktor yang mempunyai loncatan tenaga ikatan yang besar. Untuk memfabrikasi satu pengesan bio yang lebih sensitif dan pemilihan yang bagus, partikel nano emas (GNPs) telah dipilih untuk pengubahsuaian permukaan struktur nano ZnO yang kemudiannya membentuk konjugat gold-thiolate dengan ubahsuaian-thiol DNA. Dua cara telah digunakan untuk mengesan penetapan dan penghibridan DNA, iaitu analisis dielektrik dan analisis elektrokimia. Pengesanan DNA menggunakan analisis dielektrik dilakukan dengan menggunakan elektrod interdigitated emas ubahsuaian filem nipis ZnO. Pengesan yang dibina jelas membezakan sasaran dan bukan sasaran DNA melalui ukuran kapasitan, permitiviti, dan impedans. Pengesanan DNA menggunakan analisis elektrokimia dengan voltametri kitaran mengesahkan permukaan rod nano ZnO yang diubahsuai dengan (3-aminopropyl)triethoxysilane (APTES) dan partikel nano emas memberi pengesanan sasaran DNA yang lebih baik berbanding dengan yang hanya mengandungi partikel nano emas.

Fabrication and Characterization of ZnO Nanostructures for DNA Detection

ABSTRACT

Zinc oxide (ZnO), a representative of group II-IV metal-oxide semiconductor material is widely studied in the current research community. ZnO with its wide direct band-gap (3.37eV) and high exciton binding energy (60meV) providing the advantages of their electrical and optical properties. Due to these unique properties and easiness to grow using bottom-up approach combines with high isoelectric point, toxic-free, high surface-area-to-volume ratio, biosafe, and biocompatible, ZnO nanostructures have great interest in the application of biosensor. The aim of this research work is to synthesis, fabricate, and characterize ZnO nanostructures based sensor for DNA immobilization and hybridization detection. Two types of ZnO nanostructures were studied, namely thin films and nanorods (NRs). Highly transparent ZnO thin films were successfully synthesized using ease and low-cost sol-gel spin-coating method. ZnO NRs with nanoscale possessed high crystalline structure was further grown from the as-prepared thin films through low-temperature hydrothermal growth. In this thesis, we studied the influence of different solvents on the structure, optical and electrical properties of the ZnO nanostructures. Four types of solvents namely methanol, ethanol, isopropanol, and 2-methoxyethanol had been chosen for ZnO seed solution preparation. The observed results using FESEM indicated that the nanoparticles and nanorods with the size less than 40 nanometer and 60 nanometer, respectively were successfully synthesized. The investigation on optical properties using UV-Vis-NIR spectrophotometer confirmed ZnO is classified as a wide band gap semiconductor material. In order to fabricate a biosensor with high sensitivity and selectivity, a gold nanoparticles (GNPs) were selected for the surface modification of ZnO nanostructures which later formed gold-thiolate conjugation with thiol-modified ssDNA probes. Two approaches were used for the immobilization and hybridization of DNA detection, which were dielectric analysis and electrochemical analysis. DNA detection using dielectric analyzer was done on interdigitated electrodes gold modified ZnO thin films. The developed sensor clearly differentiated complementary and non-complementary of target DNA through the measurement of capacitance, permittivity, and impedance. DNA detection using electrochemical analysis with cyclic voltammetry confirmed surface ZnO NRs modified with (3-Aminopropyl)triethoxysilane (APTES) and gold nanoparticles provided better detection of target DNA in comparison with those only contained gold nanoparticles.

CHAPTER 1

BACKGROUND

1.1 Introduction

Metal-oxide-thin-films with semiconducting properties have currently received considerable attention because of their convenient and useful electrical and optoelectronic properties which are suitable for diversified applications (Fan & Freer, 1993; Ghosh et al., 2006). ZnO nanostructures, type of inorganic metal-oxide-semiconductor and derivatives of group II-VI series on periodic table, have been recently applied in various applications, such as light emitting diode (Kim et al., 2011b), gas and chemical sensor (Baratto et al., 2008; Shen et al., 2005), ultraviolet (UV) photodetector (Chai et al., 2009; Ghasempour Ardakani et al., 2012; Jun et al., 2009; Mehrabian et al., 2011), solar cell (Guillen et al., 2011; Matsubara et al., 2003) and other sensor devices.

ZnO thin films are low dimensional nanostructured materials of great interests because of their unique physiochemical properties and convenient fabrication process into various types of nanostructures, such as nanowires (NWs) (Huang et al., 2001; Usman et al., 2010), nano-flakes (Kashif et al., 2012c), nanorods (NRs) (He et al., 2011; Kashif et al., 2012b), nanoporous (Kashif et al.; Li et al., 2011), nanobelts (Li et al., 2002), nanorings (Hughes & Wang, 2005), nanocables (Kim et al., 2006), nanotubes (Ali et al., 2011b; Ren et al., 2008), nanocolumns (Park et al., 2006), nanocombs (Yang et al., 2008), nanoneedles (Zhang et al., 2005), nanosheets (Zhang et al., 2011), and nanowalls (Maeng et al., 2009). There are various methods such as sol-gel spin-coating

(Kashif et al., 2012c), chemical vapor deposition (CVD) (Li et al., 2003), physical vapor deposition (PVD) (Dutta et al., 2008; Kamaruddin et al., 2011; Wang et al., 2005a), sputtering (Deng et al., 2007), electro-deposition (Chen et al., 2006), spray pyrolysis (Ashour et al., 2006), and ink-jet printing (Shen et al., 2005) have been documented to synthesis various ZnO thin films, however, the preparation of ZnO thin films with desirable structure, optical and electrical properties are still a technological challenge.

ZnO NRs with its large surface-area-to-volume ratio make it as a potential material and structure mainly applied in sensor application. There are two types of approaches to produce ZnO NRs, namely top-down and bottom-up. However, the latter gives the advantages of better way to obtain nanostructures with fewer defects, more homogenous structure and ability to control shape and size of NRs as compared to the top-down approach. Under bottom-up approach, various techniques have been proposed to create single-crystalline and high quality of ZnO NRs, such as aqueous hydrothermal growth (Kashif et al., 2012c), metal-organic chemical vapor deposition (MOCVD) (Su et al., 2012), vapor phase epitaxy (Moriyama & Fujita, 2007), vapor phase transport (Bakin et al., 2007), and vapor-liquid-solid (VLS) method (Suh et al., 2010).

ZnO nanostructures, which have high isoelectric point (IEP) from 8.7 to 10.3, are the main feature for the low isoelectric point of DNA (5.0) to immobilize on ZnO nanostructures surface through electrostatic interaction. Due to this feature, detection of target DNA is possible done by direct measurement from electric signals, such as dielectric analysis and electrochemical measurement. In addition, lack of toxicity and high chemical stability of ZnO make it as a prospective material in biomolecule detection application (Zhu et al., 2007), such as DNA and glucose sensor (Fulati et al., 2010; Usman et al., 2010).

1.2 Overview of Nanotechnology

The word 'nano' comes from the Greek meaning extremely small or dwarf. The word 'nano' was officially used as a standard in year 1960. It is a prefixing unit often applied in engineering and science field. The term nano correspond to one-billionth of a meter or a factor of 10^{-9} . For a good example, one need to chop the human hair into 10,000 times then only manage to get 1 nm diameter of human hair (Hunt & Mehta, 2006).

Nanotechnology with the word "nano" means any technology with nanoscale which has been applied in the real world. Materials, devices or machines which build from 1 to 100 nanometers are considered as nanotechnology (Wang, 2005). The creation of functional material, device or system by controlling a matter at the scale less than 100 nm using atom or molecule is considered as a part of technology and science in nanotechnology field. There are plenty of advantages provided by nanotechnology, such as low-cost device fabrication, large surface-area-to-volume ratio of the materials, high productivity, and high efficiency of material (Jiang & Lu, 2008; Lines, 2008) which show an improvement in various applications compared to their bulk materials (Lu et al., 2006). These advantages make it becomes the most important technologies in future for various fields, such as material engineering, optical applications, sensor applications, medical applications, and biotechnology applications.

The idea of nanotechnology was first suggested by a Nobel Prize winner in physics, Richard Feynman, in a talk "There's Plenty of Room at the Bottom" (Feynman, 1960). In 1914, Richard Adolf Zsigmondy, an Austrian chemist, was the first person to characterize the particle size in nanometer (Santamaria, 2012). In 1974, Norio Taniguchi from Tokyo University of Science was first defined the term of nanotechnology (Taniguchi, 1974). After the first transistor has been built by John

Bardeen and Walter Brattain at AT&T's Bell Labs in 1947 (Grundmann, 2011), Gordon Moore, who was the co-founder and Chairman Emeritus of Intel Corporation made a prediction that the number of transistors in an integrated circuits would be doubles up approximately every two years. The name of this law was given using his name, which is Moore's law and this trend has been practically help in study for 50 years (Moore, 1965). The word 'nanotechnology' was again popularized by Kim Eric Drexler (an American engineer) in year 1980's (Eric, 1986). According to him, a machine, such as robots arms, motor or even computer is possible to build on a scale of molecules, which is only in few nanometers wide.

The synthesis and fabrication of nanomaterials are commonly divided into two main categories, which are top-down and bottom-up methods. Top-down approach is a method by breaking down a bigger size of material into nanosize material through crushing or lithography process. This kind of process mainly used in current micro-chip processor fabrication process. On the other hand, bottom-up approach involves the assembly of atoms, molecules, clusters or nanoparticles into nanosize materials or structures in a controlled manner. The bottom-up method enables miniaturization and manufacture of semiconductor product at smaller scale and desire design. There are several advantages using bottom-up method, such as ease to fabricate, low-cost, and scalable. However, this approach cause the unpredictable of growth direction and structure of nanomaterial (Hanrath & Korgel, 2002).

1.3 Problem Statement

Currently, the detection of DNA is an area of great interest as it is the key feature in the research for specific nucleotide sequences of DNA detection. This technique plays an important role in biodiagnostics (Ali et al., 2012c), determination of