SYNTHESIS AND CHARACTERIZATION OF ZnO NANOSTRUCTURES FOR ULTRAVIOLET (UV) LIGHT SENSING APPLICATION

By

QAZI MUHAMMAD HUMAYUN
(1141710585)

A thesis submitted
In fulfillment of the requirements for the degree of
Doctor of Philosophy (Nanoelectronic Engineering)

Institute of Nanoelectronic Engineering
UNIVERSITI MALAYSIA PERLIS

2014

ACKNOWLEDGEMENT

My long and hard expedition to achieve my doctorate degree will end with this thesis. It was quit impossible for me to travel this long journey alone without the kindness of Allah Almighty – the most gracious, most merciful.

I am overwhelmed with great appreciation and deep regards to my respected Supervisor Professor Dr.Uda Hashim for his worthy guidance and grant of chance to work and study at *Institute of Nano Electronic Engineering (INEE) University Malaysia Perlis.* He always took care. Without his constant encouragement, supervising and suggestions throughout the course of this thesis it was impossible to complete the research work.

I also take this opportunity to express a deep sense of gratitude to Dr. Muhammad Kashif for his cordial support, valuable information, guidance and motivation, which helped me in completing this task through various stages. He made me familiar with the nano materials research and taught me the spirit of research “to be productive, patient, novel and never give up even when the experiments go wrong at first”.

I am obliged to all the staff members of the Institute *of Nano Electronic (INEE) University of Malaysia Perlis*, for the valuable information provided by them in their respective fields. I am grateful for their cooperation and moral support during the period of my assignment.

Last, thanks to my family and friends for their constant encouragement without which this assignment would not be possible. I admit my indebtedness to my Uncle Qazi Fazal Karim, my brother Qazi Binyamin and my brother-in-law Dr Hikmat Ullah for their unconditional support and interest to carry on my learning. I pray for my late father Qazi Fazal Qayyum who always believed in me and wished for my higher studies. He would feel proud of me if he were still among us. I also wish my thanks to my Uncle Qazi Muhammad Naeem who endured the pain of proofreading and made it possible to publish.

TABLE OF CONTENTS

LIST OF TABLES

TABLE NO **PAGE**

LIST OF FIGURES

LIST OF ABBREVIATIONS

a.u	Arbitrary unit
Ag	Silver
Al	Aluminium
Ar	Argon
A	Absorption coefficient
Å	Angstrom
ahv	Optical band gap
Λ	Absorption band edge
BOE	Buffer Oxide Etch
DI	Deionized
E_g	Energy band gap
ε_∞	Optical dielectric constant
e^-	Electron
FWHM	Full-width-Half maximum
hv	Photon energy
h^+	Hole
i-t	Current-Time
I-V	Current-Voltage
JCPDS	Joint Committee on Powder Diffraction Standards
ml	Milli Litre
MSM	Metal-Semiconductor-Metal
mw	Milli Watt
µm	Micrometre
N	Refractive Index

Nm	Nanometre
O_2	Oxygen
RCA	Radio Corporation of America
rpm	Revolution Per Minute
SEM	Scanning Electron Microscope
Sn	Tin
UV	Ultraviolet
XRD	X-ray Diffraction
Zn	Zinc

LIST OF SYMBOLS

	X-ray Diffraction Angle
Ω	Ohms

SINSTESIS DAN PENCIRIAN ZnO NANO UNTUK ULTRAUNGU (UV) PERMOHONAN LIGHT SENSING

ABSTRAK

Nanoteknologi mempunyai pengaruh kuat ke atas banyak teknologi yang diketahui dengan banyak kelebihan, seperti kos rendah dan lebih besar nisbah permukaan kawasan-ke-jumlah berbanding dengan rakan sejawatannya dari sebahagian besar mereka. Antara II-IV oksida bahan semikonduktor zink (ZnO) adalah semikonduktor jenis n dengan tenaga jurang jalur 3.37 eV dan mempunyai exciton besar tenaga pengikatan ~ 60 meV. ZnO dan aloi mempunyai aplikasi peranti yang luas terutamanya dalam pembuatan diod pemancar cahaya (LED), sel-sel solar dan waveguides optik dan Ultraviolet (UV) photodetectors. Ultraviolet (UV) photodetectors digunakan secara meluas dalam pelbagai aplikasi komersial dan ketenteraan terutamanya untuk mendapatkan ruang ke ruang komunikasi, pemantauan pencemaran, pensterilan air, api penderiaan, dan peluru berpandu awal pengesanan kepulan. Berbeza dengan galium nitrida (GaN), ZnO mempunyai tertinggi tepu elektron halaju; dengan itu, photodetectors dilengkapi dengan ZnO boleh melakukan pada kelajuan operasi yang maksimum. Objektif kajian adalah untuk mendepositkan ZnO filem nipis dan nanorods ZnO melalui kaedah sol-gel di kawasan terpilih elektrod microgap jarak dan pencirian untuk ultraungu (UV) permohonan sensing. Oleh itu struktur Zerogap yang rama-rama topologi direka oleh perisian AutoCAD, dan untuk mencapai resolusi yang lebih baik semasa proses masking gambar reka bentuk itu telah berpindah kepada komersial fototopeng kaca krom. Semua kawasan terpilih didepositkan ZnO berasaskan nano sensor telah lanjut diuji untuk ultraungu (UV) permohonan sensing. Pada pendedahan ultraungu (UV) cahaya keuntungan semasa, tindak balas/masa pemulihan, kebolehulangan, kepekaan, dan reproductivity responsivity daripada fabrikasi ZnO berasaskan elektrod microgap sensor dipaparkan permohonan itu diharapkan untuk mengesan cahaya UV. Selain itu pengesanan isyarat pada voltan operasi yang rendah (1 V) mendedahkan bahawa sensor palsu boleh digunakan untuk peranti mini dengan penggunaan tenaga yang rendah. Morfologi permukaan sifat-sifat struktur, optik dan elektrik di nano ZnO disintesis telah disifatkan menggunakan SEM, XRD, dan sourcemeter masing-masing. Untuk mengkaji kesan dadah pada nano ZnO akhirnya, timah (Sn) telah dipilih, dan berjaya disintesis pada substrat kaca oleh suhu sol-gel hidroterma proses pertumbuhan yang rendah. Sebagai disintesis nanorods ZnO Sn-didopkan adalah pos disepuh lindap pada tiga suhu yang berbeza dan menyiasat kesan suhu selepas penyepuhlindapan pada struktur, sifat optik, elektrik dan fotoaktif dengan menggunakan pembelauan sinar-X, UV-Vis spektroskopi, IV dan ia ukuran. Penghabluran dan c-paksi orientasi nanorods ZnO Sn-didopkan telah meningkat dengan suhu sepuh lindap. Sebagai suhu selepas penyepuhlindapan meningkatkan nanorods ZnO Sn-didopkan menunjukkan variasi ketara setelah dicampurkan dan sfera bentuk di morfologi permukaan daripada yang pada suhu selepas penyepuhlindapan yang lebih rendah; keputusan ini menunjukkan bahawa sampel yang sangat kristal dalam alam semula jadi. Ini memberikan nilai jurang tenaga optik nanorods ZnO Sn-didopkan menurun penyepuhlindapan suhu bertambah. Ciri-ciri elektrik mendedahkan kesan suhu penyepuhlindapan pada kerintangan dan fotoaktif sifat nanorods ZnO Sn-didopkan. Oleh itu, model Herve dan Vandamme yang dicadangkan dan ultraungu baik (UV) fotoaktif sampel selepas anil terpakai dalam aplikasi peranti optoelektronik.

SYNTHESIS AND CHARACTERIZATION OF ZnO NANOSTRUCTURES FOR ULTRAVIOLET (UV) LIGHT SENSING APPLICATION

ABSTRACT

Nanotechnology has strong influence over many known technologies with plenty of advantages, such as low-cost and larger surface-area-to-volume ratio compared with their bulk counterpart. Among II-IV semiconductor materials zinc oxide (ZnO) is an n-type semiconductor with band gap energy of 3.37 eV and having large exciton binding energy of ~ 60 meV. ZnO and its alloys have vast device applications mainly in manufacturing of light emitting diodes (LEDs), solar cells, optical waveguides and Ultraviolet (UV) photodetectors. Ultraviolet (UV) photodetectors are widely used in various commercial and military applications, especially to secure space-to-space communications, pollution monitoring, water sterilization, flame sensing, and early missile plume detection. In contrast to gallium nitride (GaN), ZnO has a highest electron saturation velocity thus, photodetectors equipped with ZnO can perform at a maximum operation speed. The objective of research is to deposit ZnO thin film and ZnO nanorods by sol-gel method at selective area of microgap electrodes spacing and characterization for ultraviolet (UV) sensing application. Therefore the Zerogap structure of butterfly topology was designed by AutoCAD software, and to achieve the better resolution during photo masking process the design was transferred to commercial chrome glass photomask. All the area selective deposited ZnO based nano-sensors were further tested for ultraviolet (UV) sensing application. On exposure of ultraviolet (UV) light the current gains, response/recovery times, repeatability, sensitivity, reproductivity and responsivity of the fabricated ZnO based microgap electrodes sensors displayed the promising application for UV light detection. Moreover the signal detection at low operating voltage (1 V) revealed that fabricated sensors can be used for miniaturized devices with low power consumption. The surface morphologies structural, optical and electrical properties of the synthesized nanostructures ZnO were characterized using SEM, XRD, and sourcemeter respectively. To study the doping effect on ZnO nanostructures finally, tin (Sn) was selected, and successfully synthesized on glass substrate by low temperature sol-gel hydrothermal growth process. The as synthesized Sn-doped ZnO nanorods were post annealed at three different temperatures and investigated the effect of post-annealing temperatures on structural, optical, electrical and photoresponse properties by using X-ray diffraction, UV-Vis spectroscopy, I-V and i-t measurements. The crystallinity and c-axis orientation of Sn-doped ZnO nanorods were increased with annealing temperatures. As post-annealing temperature increased the Sn-doped ZnO nanorods showed noticeable variations having agglomerated and spherical shape at surface morphology than those at a lower post-annealing temperature; this result indicates that the samples are highly crystalline in nature. The optical bandgap energy of Sn-doped ZnO nanorods decreased as annealing temperature increases. Electrical characteristics reveal the effect of annealing temperature on resistivity and photoresponse properties of Sn-doped ZnO nanorods. Hence, the proposed Herve and Vandamme model and the improved ultraviolet (UV) photoresponse of post-annealed samples are applicable in optoelectronic device applications.

CHAPTER 1

BACKGROUND

BACKGROUND

1.1 Introduction

The overview for present thesis is divided into five sections, namely ZnO properties application, problem statements, research objectives, research scope and thesis outline.

1.1.1 Nanomaterials

During the last few decades, nanomaterials have been the subject of extensive interest because of their potential use in a wide range of fields like, optoelectronics, catalysis and sensing applications (Jain, A., et. al. 2006). Due to smaller size and larger surface area to volume ratio, nanomaterials comprised novel physical and chemical properties that are difficult to observe in conventional and bulk counterparts. Generally there are three types of nanomaterials (one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D)) have been fabricated. Presently, nanomaterials (Ornelas, R. E. et. al., 2012) based research areas are rapidly expanding and growing. Moreover metal oxide based nanomaterials have drawn a special attention because of attractive properties coupled with efficient flexibility in structures. Not only the fascinating properties of these metal oxide nanostructures from their bulk like, photodetection, chemical sensing and piezoelectricity are inheriting but also have properties related to size confinement and their highly anisotropic geometry (Comini, E. et., al, 2009). An important issue in research development and industrial standpoints is to investigate conventional and new properties together with unique effects of nanostructures, which open the opportunity towards future novel metal oxide nanostructures fabrication.

1.1.2 Zinc Oxide

Zinc oxide (ZnO) nanostructures posses great attention, among various metal oxides nanostructures because of its novel properties and application (Ajili, M. et. al., 2013; Saif, M. et. al., 2013; Zhang, J. et. al., 2013; Xie, G. C. et. al., 2012; Xia, X. H. et. al., 2010; Xiao, X. et. al., 2010; Xie, C. et. al., 2010; Samaele, N. et. al., 2010; Wang, D. et. al., 2009; Yadav, B. C. et. al., 2009; Zhang, H. et. al., 2009; Badadhe, S. S. et. al. 2009; Salunkhe, R. R. et. al., 2009; Abramova, V. et. al., 2009; Vigil, O. et. al., 2000). It is existed compound in group II-VI of approximately 3.2 eV to 3.4 eV direct band gap energy at ambient temperature (O'Brien, S, et. al., 2008; Singh, P. et. al., 2007; Srinivasan, G. et. al., 2006; Lee, J.-H. at. al., 2004; Whangbo, S W, et. al. 2000). Its melting point (1975 ^{o}C) suggest strong bonding and show thermally and chemically resist materials (Norton, D. P. et. al., 2004; Olvera, M. d., et. al., 2000). In alkalis, acids and water it is completely soluble.

Physically ZnO ‘’Zinc Oxide’’ is existed in white powder form. Natrurally ZnO exibit n-type conductivity, while its p-type conductivity can be generated by special synthesis process. Generally n-type conductivity might because of intrinsic defects and oxygen vacancies (Sahoo, T. et. al. 2010; Kang, H. S. et. al., 2008). N-type conductivity of ZnO could be activated by adding different doping elements such as Indium (In), Boron (B), Aluminium (Al), and Gallium (Ga) (Caglar, Y. et. al., 2007; Park, S. M. et. al., 2006; Pawar, B. N. et. al., 2005; Musat, V. et .al., 2004). The ZnO crystals are normally stable and found in wurtzite structure or hexagonal symmetry (Takali, F. et. al., 2011). Lattice parameters ratio c/a= 1.602 (where a=0.3249 nm and c= 0.5207 nm are lattice parameter of ZnO at 3000 K) suggests that ZnO is an ideal closed packed hexagonal structure (1.633) (Kang, H. S. et. al., 2008; Caglar, Y. et. al., 2007; Park, S. M. et. al., 2006; Pawar, B. N. et. al., 2005; Musat, V. et .al., 2004). Wurtzite (hexagonal) structure of ZnO contains zinc (Zn) atoms which are tetrahedrally coordinated to four oxygen (O) atoms where the Zn d-element hybridize with O p-electrons (Klingshirn, C. et., 2009). The (0001), (000-1), (11-20) and (10-10) are the most important common faces of wurtzite ZnO. Polar Zn terminated basal plane is (0001), while (000-1) called polar O terminated plane. The positively and negatively charged polar surfaces because of Zn and O terminated plane (Zhong Lin Wang. et. al., 2006), moreover the non polar plane (11-20) and (10-10) contains Zn and O atoms in equal numbers. The (11-20) and (10-10) are non polar planes which contains an equal number of Zn and O atoms. Along hexagonal axis, polar symmetry is due to tetrahedral coordination and responsible for ZnO properties such as piezoelectricity, spontaneous polarization, defect formation, etching and crystal growth. Conduction band (CB) of ZnO arises from Zn^{++} 4s orbital (symmetry), and upper valence bands (VB) from the O^{--} 2p states with an admixture of Zn^{++} 3d levels (Zhang, C. h. et. al., 2012; Yang, X. et. al., 2011; Klingshirn, C. et. al., 2009). At same axis of brillouin zone valence band maxima and conduction band minima occurred to indicate that ZnO is direct semiconductor material (Zhang, J. et. al., 2013; Varnamkhasti, M. G. et. al., 2012; Wang, C.-K. et. al., 2012; Yadav, B. C. et. al., 2012; Xie, L. H. et. al., 2012; Hafdallah, A. et. al., 2011; Hakim, A. et. al., 2009; Wang, D. et. al., 2009; Hakim, A. et. al., 2009; Sagar, P. et. al., 2007; Santos-Cruz, J. et. al., 2005; Sagar, P. et. al., 2005).

In one-dimension scale; ZnO nanorods is an attractive components compared with other nanostructures for nanoscale electronic, photonic device manufacturing, and in biomedical device application (Xu, S. et. al., 2011; Kishwar, S. et. al., 2010; Calavia, R. et. al., 2010). Furthermore ZnO nanorods can be grown easily using variety of substrates such as semiconductor, metal surface, plastic, disposable paper and glass, etc (El-Nahass, M. M. et. al., 2012; Zainelabdin, A. et. al., 2010; El-Hagary, M. et. al., 2010; Manekkathodi, A. et. al., 2010; Bano, N. et. al., 2010; Postels, B, et. al. 2007).

1.1.3 Synthesis of ZnO Nanostructures

ZnO can be synthesized by variety of different techniques with different morphologies, such as pulsed laser deposition (PLD), sputtering, chemical vapor deposition (CVD), sol-gel, metal organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) (Habibi, M. H. et. al., 2013; Gurav, K. V. et. al., 2010 Srinivasan, G. et. al., 2008; Park, S. H. et. al., 2007; Kuo, S. Y. et. al., 2006; Gupta, V. et. al., 2006; Deng, H. et. al., 2004; Ogata, K. et al., 2000). The good quality crystal can be produced by MOCVD and MBE technique but the systems are expensive and need complicated maintenance. From sputtering and pulsed laser deposition technique one can produce good and high quality ZnO crystal but the requirement of vacuum chamber, high quality target, rigid experimental condition such as controlled gas atmosphere, vacuum and cleaning make this technique difficult for implementation (Jimenez Gonzalez, A. E. et. al., 1998). Although by chemical vapor deposition technique, good quality ZnO can be produced but the system need carrier gas argon (Ar) and high temperature for operation and optimization to large scale deposition finally increase the product cost. Among them sol-gel is the best technique for ZnO preparation, it is low cost, need low temperature and can be implemented for large scale preparation as compared with other techniques (Sagar, P. et. al., 2005). Moreover by sol-gel ZnO of good quality could be produced, which can be expected to use for electronic device application and in industry (Pal, N. et. al., 2013; Varnamkhasti, M. G. et. al., 2012; Zhang, Y. et. al., 2012; Xu, C. H. et. al., 2011; Yakuphanoglu, F. et. al., 2010; Sagar, P. et. al., 2005; Santos-Cruz, J. et. al., 2005; Yamamoto, T. et. al., 2004).

1.1.4 Sol-gel Process

The sol-gel is a wet chemical procedure in which a solution of metal compound or a suspension of very fine particles in a liquids (referred to as a sol) is converted into a semi rigid-mass (a gel) (Guo, Yeping. et. al., 2002). The sol-gel consists of mixture of solid materials suspended in a liquid solution. Gel occurs when the individual molecules from structures which then form molecules matrix network that are same with the formation of semiconductor crystal but without order spacing. Moreover between the particles the pores are formed by this process. Depending on temperature, process and time the molecule matrix becomes dense and large. The final materials properties, including structural, optical and electrical could be determine from the thin film deposition parameters like deposition speed, deposition time, drying time and drying temperature. Also low processing temperature, purity of materials and homogenous deposition make sol-gel an attractive technique. Sol-gel process can be implemented for materials preparation in variety of form such as ceramic fibers, microporous inorganic memberance, thin film, powder and extremely porous materials (aerogels).

1.1.5 Selective Area ZnO Growth

The nanomaterials properties strongly depend on their shapes and dimensions (Vasanthi, M. et. al., 2012; P. et. al., 2011; Wan, L. et. al., 2010; Selmi, M. et. al., 2008; Wagener). It is significantly important to control the periodicity, pattern, orientation, well aligned and order shape at selective area on sample substrate for development of novel micro-nano scale (nanostrucutres ZnO) devices. Therefore various techniques have been developed for well aligned growth of ZnO nanostructures e.g metal organic chemical vapors deposition, solution based and physical vapor deposition method (Lyu, S. C. et. al., 2003; Park, W. I. et al., 2002). The solution based methods is low cost, simple, need low temperature and also scalable for large areas.

1.1.6 Optical Properties of ZnO

The ZnO exhibits UV emission, UV absorption also transparent to visible light (Huang, B. et. al., 2008; Sun, Y. et. al., 2006; Kim, Y.S. et al., 2005). Due to direct and wide band gap semiconductor materials, ZnO is considering good candidate for electronic device application. Properties of direct and wide band gap allow ZnO to function at high break down voltages, low noise, high temperature and power (Xu, Jin. et. al., 2004). Such characteristics could enhance the application of ZnO for light emitting application mainly blue and ultraviolet light emission diodes. High exciton binding energy (60 meV) of ZnO shows the light emission efficiency at room temperatures (Lee, J. H. at. al., 2004). Moreover for solar cell technology transparency properties of ZnO allow to use as transparent electrodes.

1.1.7 Ultravoilet (UV) Light and its Application

The electromagnetic radiation in spectral range of 180 to 400 nm is called ultraviolet (UV) light radiation. Immediate and long time UV light exposure causes eye injury, skin burn and skin cancer. Outdoor working peoples especially workers suffer the direct UV exposure on their bodies. While the remaining peoples may be exposed to UV radiation from non-solar sources, among them some emits high intense UV radiation like; high intensity discharge lamps, curing of paints, ink mercury vapor lamps and from arc of welding (Lupan. et. al. 2014). Due to sun entitle angle nearer to equator, UV radiations are