SYNTHESIS AND CHARACTERIZATION OF ZINC OXIDE/COPPER OXIDE CORE-SHELL HETEROJUNCTION NANOWIRES GROWN BY VAPOR DEPOSITION

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A thesis submitted in fulfilment of the
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DEDICATION

Specially dedicated to my beloved parents, my family and my friends for their patience, support, prayers, encouragement, and blessings.

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ABSTRACT

This thesis investigates the controlled growth and vertically aligned ZnO/CuO core-shell heterojunction nanowires (NWs) formation by vapor deposition and oxidation approach. ZnO/CuO heterostructure nanowires were grown on n-type Si substrate using modified thermal chemical vapor deposition (TCVD) assisted by sputtering deposition followed by thermal oxidation under controlled growth conditions. The effects of fabrication parameters on structure, growth mechanism, optical and electrical properties of the ZnO/CuO core-shell heterojunction were thoroughly investigated. Structural characterization by field emission scanning electron microscope (FESEM), high resolution transmission electron microscope (HR-TEM), scanning transmission electron microscope (STEM), X-ray photoelectron spectroscope (XPS), X-ray diffractometer (XRD) and energy dispersive X-ray (EDX) reveals that a highly pure crystalline ZnO core and polycrystalline CuO shell were successfully fabricated in which ZnO and CuO are of hexagonal wurtzite and monoclinic structures, respectively. The growth of ZnO nanowires is along the c-axis [002] direction and the nanowires have relatively smooth surfaces with diameters in the range of 35-45 nm and lengths in the range of 700-1300 nm. The CuO nanoshell with thickness of around 8-10 nm is constructed of nanocrystals with sizes in the range of 3–10 nm. EDX spectrum, elemental mapping and high angle annular dark field (HAADF) STEM confirmed that the NW compositions were Zn, Cu and O. Photoluminescence (PL) study shows the enhancement of intensity ratio and decrease in the energy band of ZnO/CuO core-shell heterojunction NW arrays that might be very useful in photocatalysis, light emission devices and solar energy conversion applications. Similarly, UV-VIS-NIR spectroscopy study shows that the grown ZnO NW arrays have a maximum reflectance of approximately 42% in the 200 to 800 nm range while the ZnO/CuO core-shell heterojunction NW arrays have a decreased value of 24%. This means that the absorption efficiency of ZnO/CuO core-shell heterojunction nanowire arrays clearly shows a higher absorption compared to pure ZnO nanowire arrays. Besides, the good rectifying behavior of ZnO/CuO core-shall NW by conductive AFM (C-AFM) showed that p-n junction was successfully fabricated. Furthermore, from the XPS analysis, the measured values for valence band offset (VBO) and conduction band offset (CBO) were found to be 2.4 eV and 0.23 eV, respectively for the fabrication of ZnO/CuO core-shell heterojunction NWs. It was observed that ZnO/CuO core-shell heterojunction NWs have type-II band alignment. This study obviously suggests that using the controlled growth mechanism, it is possible to control crystal structure, surface morphologies and orientation of the core-shell NW arrays.

ABSTRAK

Tesis ini menyiasat pertumbuhan terkawal dan pembentukan teras-petala simpangan hetero dawai nano (NW) ZnO/CuO jajaran menegak dengan pendekatan pemendapan wap dan pengoksidaan. Dawai nano struktur hetero ZnO/CuO ditumbuhkan di atas substrat Si jenis-n nenggunakan pemendapan terma wap kimia (TCVD) yang diubah suai dibantu oleh pemendapan percikan diikuti dengan pengoksidaan terma di bawah keadaan pertumbuhan terkawal. Kesan parameter fabrikasi terhadap struktur, mekanisme pertumbuhan dan sifat-sifat optik dan elektrik bagi teras-petala simpangan hetero ZnO/CuO telah disiasat dengan menyeluruh. Pencirian struktur dengan mikroskop elektron pengimbas pemancaran medan (FESEM), mikroskop elektron penghantaran resolusi tinggi (HRTEM), mikroskop elektron penghantaran imbasan (STEM), spektroskop fotoelektron sinar-X (XPS), pembelau sinar-X (XRD) dan spektroskop serakan tenaga sinar-X (EDX) menunjukkan bahawa kristal teras ZnO yang sangat tulen dan polihabluran petala CuO telah berjaya difabrikasi di mana ZnO dan CuO masing-masing adalah berstruktur heksagon wurtzite dan monoklinik. Pertumbuhan dawai nano ZnO adalah sepanjang arah paksi–c [002] dan dawai nano mempunyai permukaan yang licin dengan diameter dalam julat 35-45 nm dan dan panjang dalam julat 700-1300 nm. Petala nano CuO dengan ketebalan sekitar 8-10 nm dibina daripada nanokristal dengan saiz dalam julat 3-10 nm. Spektrum EDX, STEM pemetaan unsur dan anulus medan gelap bersudut tinggi (HAADF) dan STEM mengesahkan bahawa komposisi NW ialah Zn, Cu dan O. Kajian photoluminescence (PL) menunjukkan peningkatan nisbah keamatan dan pengurangan jalur tenaga tatasusunan NW simpangan hetero teras-petala ZnO/CuO yang berkemungkinan sangat berguna dalam aplikasi fotomangkin, peranti pemancar cahaya dan penukaran tenaga solar. Begitu juga, spektroskopi UV-VIS-NIR menunjukkan bahawa tatasusunan NW ZnO yang ditumbuhkan menghasilkan pantulan maksimum kira-kira 42% dalam julat 200-800 nm manakala tatasusunan NW simpangan hetero teras-petala ZnO/CuO telah berkurangan kepada 24%. Ini bermakna tatasusunan NW simpangan hetero teras-petala ZnO/CuO menunjukkan kecekapan penyerapan lebih tinggi berbanding tatasusunan NW ZnO tulen. Selain itu, sifat membetulkan NW teras-petala ZnO/CuO yang baik menunjukkan yang persimpangan p-n telah berjaya difabrikasi. Tambahan pula, dari analisis XPS, telah ditemui nilai diukur bagi ofset jalur valens (VBO) dan ofset jalur konduksi (CBO) masing-masing ialah 2.4 eV dan 0.23 eV, untuk fabrikasi NW simpangan hetero teras-petala ZnO/CuO. Didapati bahawa penjajaran jalur bagi NW simpangan hetero teras-petala ZnO/CuO adalah jenis-II. Kajian ini jelas menunjukkan bahawa dengan menggunakan mekanisme pertumbuhan dikawal, terdapat kemungkinan untuk mengawal struktur kristal, morfologi permukaan dan orientasi teras-petala tatasusunan NW.

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LIST OF ABBREVIATIONS

Ar	-	Argon
CVD	-	Chemical Vapor Deposition
CuO	-	Copper Oxide
C-AFM	-	Conductive Atomic Force Microscopy
CB	-	Conduction band
CBO	-	Conduction band offset
CSNano	-	Centre for Sustainable Nanomaterial
CL	-	Core-Level
E_g	-	Band gap
eV	-	Electron volt
FTM	-	Film Thickness Monitor
FE-SEM	-	Field Emission Scanning Electron Microscopy
HS	-	Heterostructure
HRTEM	-	High-Resolution Transmission Electron Microscopy
I-V	-	Current-voltage
MFC	-	Mass Flow Controller
NWs	-	Nanowires
NRs	-	Nanorods
nm	-	Nanometers
NIR	-	Near infrared
O_2	-	Oxygen
PVD	-	Physical Vapor Deposition
PL	-	Photoluminescence
PECVD	-	Plasma Enhanced Chemical Vapor Deposition
SAED	-	Selected Area Electron Diffraction

STEM	-	Scanning Transmission Electron Microscopy
Si	-	Silicon
sccm	-	Standard cubic centimeter per minute
TCVD	-	Thermal Chemical Vapor Deposition
TEM	-	Transmission Electron Microscopy
UV	-	Ultra-Violet
UV-Vis	-	Ultra-Violet Visible
VB	-	Valance band
VBM	-	Valance Band Maximum
VBO	-	Valance band offset
VLS	-	Vapor-Liquid-Solid
VS	-	Vapor-Solid
XRD	-	X-rays Diffraction
XEDS	-	Energy Dispersive X-rays Spectroscopy
XPS	-	X-ray Photo-electron Spectroscopy
ZnO	-	Zinc Oxide
Zn	-	Zinc

LIST OF SYMBOLS

T	-	Absolute Temperature
n	-	Ideality Factor
k_B	-	Boltzmann constant
I_S	-	Reverse saturation current
q	-	charge on electron
V	-	Applied Voltage
m	-	slope of straight line
Φ	-	Work function

APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background

In recent years the research on one-dimensional (1D) nanostructures of different materials for their remarkable performance and properties have been increasing and has gained much attention for the device fabrication due to their size and shape dependent properties. This is the unique reason that nanostructures have exceptional properties as compare to the bulk materials properties. This is due to the dependence of the physical properties and chemical properties of one-dimensional nanostructures on size and shape. One-dimensional nanostructures, including nanowires (NWs) and nanorods (NRs) are the most studied nanomaterials for their important future application prospects. High aspect ratio, extremely large surface area as compared to volume ratio, high porosity and direct conduction path of nanowires and nanorods are the important key factors compared with other nanostructures materials. These properties of nanostructure would lead to potential use for advanced applications in photonic and nano-optoelectronics like field emission devices, nanogenerators, photovoltaics, sensing, storage devices and efficient energy conversion (Jie *et al.*, 2010; Dhara and Giri, 2013; Sun, 2015).

Semiconductor nanowires has become one of the most active area of research within the science, engineering and technology (Fan and Lu, 2005; Yi *et al.*, 2005;

Zhang *et al.*, 2012; Khan and Sakrani, 2014). Many materials are under focus with the potential of developing nano-systems and their combine heterostructure. The optimization of the performance is the main challenge at the moment. The materials to be discussed are copper oxide (CuO), zinc oxide (ZnO), and their core-shell heterojunction. To grow the nanowires of these materials and their heterojunction nanowires both high temperature methods and low temperatures methods are being extensively used.

Copper oxide (CuO) is an attractive p-type material with semiconducting property of direct band gap 1.2 eV and good absorption coefficient. Due to the intrinsic, stable, direct band gap and p-type nature properties make CuO good candidate for electrical, optical, sensing, catalysts, photovoltaic and optoelectronics devices (Xu *et al.*, 2004b; Cheng *et al.*, 2008; Jung *et al.*, 2011; Liang *et al.*, 2011; Wang *et al.*, 2011a; b; Anandan *et al.*, 2012; Chang and Yang, 2012; Filipič and Cvelbar, 2012; Willander *et al.*, 2012). 1D nanowires / nanorods of CuO synthesized by various growth techniques such as thermal decomposition of CuC_2O_4 precursors (Raksa *et al.*, 2005), hydrothermal decomposition route (Kim *et al.*, 2014), self-catalytic growth process (Chen *et al.*, 2003), and so forth. In comparison to various synthesizing methods, thermal annealing or thermal oxidation of copper foil using hot tube vacuum thermal evaporation method is a simple, convenient, and the fast method for synthesis nanostructures. Due to large surface areas CuO NWs are greatly desirable. In CuO NWs large surface areas need to high absorption of photons for greater efficiency in photovoltaic devices (Bao *et al.*, 2009; Kargar *et al.*, 2013a; Pal *et al.*, 2015), which are used for catalysis and gas-sensing (Chang and Yang, 2012). In addition CuO NWs can be potentially applicable in gas sensing, magnetic storage media, in nano-devices for catalysis and for field emitter devices (Liang *et al.*, 2011)

Similarly Zinc Oxide (ZnO) is n-type metal oxide semiconductor and is very popular due to easiness of growing it in the nanostructure form. ZnO material possesses both semiconducting and piezoelectric properties (Cha *et al.*, 2008; Aziz *et al.*, 2014). ZnO due to its popular material has different growth morphology, such as nanowires, nanorods, nanotubes, nanofibers, nanospheres and nano-tetrapods, nanocabbage, nanocombs, nanowalls and nanoprisms (Wang, 2004). These growth morphologies have been successfully grown by different methods. Most of the techniques have high temperature and long time required for the reaction. The growth techniques of ZnO nanostructure include Hydrothermal methods (Azlinda *et al.*, 2011), vapour-liquid-solid (VLS) technique (Zhang *et al.*, 2012), catalysed metal Chemical Vapour Deposition (Yi *et al.*, 2005), thermal chemical vapour deposition (Cha *et al.*, 2008), plasma enhanced CVD (Liu, 2004), oxidation method (Khanlary *et al.*, 2012), thermal evaporation (Suhaimi *et al.*, 2014) and laser-ablation (Son *et al.*, 2007).

ZnO nanostructures have many diverse applications in nano-optoelectronics, sensors, transducers, piezoelectric elements for nano-generators, sunscreens and biomedical science, since it is a bio-safe material (Wang, 2004; Fan and Lu, 2005; Schmidt-Mende and MacManus-Driscoll, 2007; Li *et al.*, 2008; Pan and Zhu, 2009; Ahmad *et al.*, 2011; Zhang *et al.*, 2012; Wei *et al.*, 2012; H. Asif, 2013; Sun *et al.*, 2014; Zhan *et al.*, 2015). The direct wide band gap of ZnO ~ 3.4 eV is suitable for optoelectronic applications due to its short wavelength. ZnO naturally exhibits n-type semiconductor, while polarity due to native defects such as oxygen vacancies and zinc interstitials. P-type doping of ZnO is still a challenging problem that is hindering the possibility of a p-n homojunction ZnO devices (Janotti and Van de Walle, 2009).

Recently the fabrication of heterostructure (HS) nanowires is being deeply studied in order to accomplishment the important properties of heterojunction of different materials. Using heterojunction nanowires approach, researchers are able to modify/improve the selective property of the oxide nanowires. Oxide nanowires are expected to have improved charge collection efficiency because of the lower interval and higher contact area between the p-type and n-type materials. ZnO NWs radial heterostructure (core-shell) have been reported using several organic/and inorganic materials (Plank *et al.*, 2008; Wang *et al.*, 2010, 2011b; Lin *et al.*, 2012; Dhara *et al.*, 2013; Chu *et al.*, 2014; Pradel *et al.*, 2016) . Several new approaches have been used for the synthesis of ZnO nanowires based on the radial heterostructures. The radial heterostructures of ZnO NWs basically consist of core-shell nanowires, which have ZnO as a core material, while a thin layer consist of a shell as a secondary material. The thin shell layer as a secondary element has a strong impact on the properties of the nanowires; however, individual property of the shell layer is not specific. These HS shows significant improvement on certain properties, mainly photophysical properties, like absorption, electron–hole pair generation and recombination rates. Although the HS are superior for modulation of certain properties, control on the external layer and formation of high quality interface between the external material and NW are, however, challenging issues.

Consequently, there is a lot of interest in the fabrication of one dimensional (1D) ZnO/CuO core-shell heterojunction nanowires for optoelectronic and nanoelectronic devices applications. As these core-shell heterojunction nanowires are expected to have improved charge collection efficiency because of the lower interval and higher contact area between the p-type and n-type materials (Cao *et al.*, 2012). Different techniques have been combined and developed to grow ZnO/CuO core-shell NWs heterojunction including chemical reactions from aqueous solutions (e.g. electrodeposition, hydrothermal growth), and vapor phase methods (chemical vapor deposition through vapor-liquid-solid (VLS) or vapor-solid (VS) growth mechanisms), Lithography and electrospinning processes and template-directed methods (Mieszawska *et al*., 2007; Fang *et al*., 2009; Hochbaum and Yang, 2010; Cao *et al*., 2012). In general, to synthesize one dimensional nanoscale heterostructures or core-shell heterostructure all these methods can be applied very carefully by manipulating the experimental growth parameters, such as source materials, pressure, temperatures and deposition time etc.

1.2 Problem Statement

Research shows that ZnO/CuO core–shell nanowire (NW) heterojunction have been studied in recent years, with emphasize generally on their synthesis and properties which are interesting and potentially useful for developing new challenging devices due to their high interfacial area, allowing for more electron-hole formation or recombination (Wang and Lin, 2009; Wang *et al.*, 2011b; Hsueh *et al.*, 2012; Kargar *et al.*, 2013b; Sun, 2015). The shell formation of copper oxide (CuO) to vertically aligned ZnO NW arrays has been reported as an especially attractive platform for opto-electronic applications because of promising p-type semiconductor having narrow band gap energy (1.2 eV) and strong absorption of the solar spectrum (Kim *et al.*, 2014).

Different techniques have been developed to grow ZnO/CuO core-shell NWs heterojunction including chemical reactions from aqueous solutions (e.g. electrodeposition, hydrothermal growth) and chemical vapor deposition (CVD) through vapor liquid solid (VLS) or vapor-solid (VS) growth mechanisms (Wang and Lin, 2009; Liao *et al.*, 2011; Wang *et al.*, 2011b; Wu *et al.*, 2013). However, these techniques have limitations to develop cost-effective and efficient nanomaterials at commercial levels. The chemical reaction method in aqueous solution needs a predeposited seed layer, and the aqueous environment tends to produce very short nanowires with low crystallinity, which is not suitable for high performance nano-devices fabrication (Zhan *et al.*, 2015). Similarly, to grow high-crystallinity core-shell nanowires heterojunction using high-temperature methods on a Si substrate needed a layer of gold film as a catalyst (Pan *et al.*, 2011). The usage of metal catalyst tends to make impure the final synthetic products and potentially impacting the electrical and optical performance.

The limited combined use of core-shell compositions in nanostructured materials highlights the lack of versatility in current synthetic techniques and emphasizes the need for new synthetic techniques to address unmet challenges facing the photovoltaic community. Further examination showed that less study has been available on CuO absorber layers (shell formation) synthesized by thermal oxidation of copper nanofilm by a thermal chemical vapor deposition method in a horizontal quartz glass reactor compared to widely used chemical methods. Therefore, it is of great importance to explore new approach to improve the properties of CuO shell formation or absorber layer properties under vapor solid (VS) grown mechanism. This would be helpful to produce good p-n junction with ZnO NW arrays with controlled morphology. A modified thermal CVD followed by sputtering and thermal oxidation methods are proposed which will result in quality of the controlled growth and vertically aligned large-area ZnO/CuO core–shell nanowire (NW) heterojunction. The corresponding structural, optical, electrical and their band offsets properties are expected to improve significantly.

1.3 Research Objectives

The objectives of this research are:

i) To synthesize ZnO and CuO nanowires by thermal CVD and thermal oxidation methods respectively and measures its properties.
ii) To produce ZnO/CuO core-shell heterojunction nanowire arrays using thermal CVD followed by sputtering and thermal oxidation methods.
iii) To measure current-voltage (*I*-*V*) of this nanowire heterojunction.
iv) To measured valance band offset of ZnO/CuO heterojunction by X-ray photoelectron spectroscopy (XPS).

1.4 Scope of the Study

The scope of this research are devoted to the development of controlled growth, vertically aligned ZnO, CuO and their core-shell (ZnO/CuO) heterojunction nanowires (NWs) and investigation of structural, optical, electrical and their valance band offset measurement properties at ZnO/CuO heterointerface.

The research work has been carried out for the selected materials keeping in view of their technological importance and mainly focus on the growth of ZnO and ZnO/CuO NWs. To produce vertically aligned ZnO/CuO core-shell heterojunction nanowires (NWs), several steps are used and each step is need on benefits and boost on the information bring into being in the previous steps. These are highlighted in the experimental section. Modified thermal chemical vapor deposition (CVD) assisted sputtering techniques followed by thermal oxidation method under controlled growth conditions are employed to prepare ZnO/CuO core-shell heterojunction nanowires on n-type Si substrate. Different deposition parameters such as; sputtering deposition time, oxygen partial pressure and oxygen flow rate are applied to investigate the growth process and surface evolution of ZnO/CuO core-shell heterojunction nanowires. The morphology and crystal structure of the as-grown ZnO nanowires and core-shell heterojunction NW arrays were characterized by field emission scanning electron microscope (FESEM, SU8020, HITACHI), high-resolution transmission electron microscopy (HRTEM, TECNAI G2 20 S-TWIN, FEI 200kV) including special feature of STEM and EDX, X-ray diffractometer (XRD) (Bruker AXS D5005, Cu Kα radiation), X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD) and Raman spectrometer (HORIBA).

The optical property of the ZnO NWs and their core-shell heterojunction NWs has been analyzed for the prepared samples at room temperature by using Photoluminescence (PL), UV visible Reflectance spectroscopy (UV-Vis-NIR Spectrometer). The electrical measurements (*I*-*V* characteristic) and rectifying behavior of ZnO/CuO core-shell heterojunction NWs about the junction development at interface were studied by Conductive Atomic Force Microscopy (CAFM). Also the energy band alignment of the core-shell heterostructure nanowire i.e valance band offset (VBO) and conduction band offset (CBO) were found experimentally from X-ray photoelectron spectroscopy.

1.5 Significance of the Study

Semiconductor nanowires are exclusively interesting having deep impact on nanoscience studies and nanotechnology application. It has been determined that one dimensional (1-D) materials exhibit remarkable nano-optoelectronic, thermal and mechanical properties as compared to bulk materials/ two dimensional thin film semiconductors. This is the unique reason that nanostructures have exceptional properties as compare to the bulk materials properties. This is due to the dependence of the physical properties and chemical properties of one-dimensional nanostructures on size and shape. Among the 1-D nanostructures, 1-D heterostructures with modulated compositions and interfaces have recently become of particular interest with respect to potential applications in nanoscale building blocks of future optoelectronic devices and systems. Consequently, there is a lot of interest in the fabrication of one dimensional (1D) ZnO/CuO core-shell heterojunction nanowires for optoelectronic and nanoelectronic devices applications. As these core-shell heterojunction nanowires are expected to have improved charge collection efficiency because of the lower interval and higher contact area between the p-type and n-type materials. The results of this dissertation research will be benefit for understanding in the properties of ZnO/CuO core-shell heterojuction nanowires to meet the requirements of using heterostructure nanaowires in developing high performance opto-electronic devices.

1.6 Organization of Thesis

The complete research work of this dissertation is organized into a five-chapter. Chapter 1 begins with the introduction, followed by the research background, the statement of the research problem, research objectives, scope of the study, and significance of this research and organization of the study.

Chapter 2 presents literature survey of ZnO, CuO and their heterostructure nanowires, growth techniques including vapour transport growth, chemical vapour deposition, thermal chemical vapour deposition and physical vapour deposition. Then it’s followed by electrical properties of semiconductor nanowires by conductive AFM and valance band offset measurement by X-ray photoelectron spectroscopy for these heterostructure nanowires.

Chapter 3 is focused on the details of the experimental procedures, which cover sample preparations of ZnO and CuO NWs fabricated by thermal chemical vapour deposition (CVD) and thermal oxidation techniques respectively, while ZnO/CuO Core-Shell heterojunction nanowire arrays were fabricated on a silicon substrate through vapor-solid (VS) mechanism without using any catalyst or seed layer via thermal CVD followed by sputtering and thermal oxidation. A brief description of sample characterization is also discussed in chapter 3.

In the next Chapter 4, reports on the results and discussion of the characterization part of the synthesised nanowires (CuO, ZnO and their ZnO/CuO core-shell heterojunction NWs) are presented. To grow these nanowires and their core-shell heterojunction nanowires successfully, various growth parameter were studied. The growth mechanism were explained, and the structural, electrical, optical and their energy band offsets properties of ZnO/CuO core-shell heterojunction NWs were performed

Finally, in chapter 5, conclusions that are evident from the work results are summarized and accompanied by a short outlook, which may boost additional efforts in this exciting and promising field.

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