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PHYSICAL AND OPTICAL PROPERTIES OF ZINC OXIDE MICRO AND NANO STRUCTURES DEPOSITED ON VARIOUS SUBSTRATES

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By

AHMAD KAMALIANFAR

Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the degree of Doctor of Philosophy

January 2014

DEDICATIONS

This thesis is dedicated to

My beloved wife and daughters for their endless patients

And my mother and father for kindness and devotion

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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Chairman : Professor Abdul Halim Shaari, PhD
Faculty : Science

This thesis attempts to investigate some unknown properties of ZnO micro- and nanostructures as one of the most promising materials in this decade. Additionally, the interaction between the components consisting of ZnO, buffer layers and substrates can produce new physical properties which may provide some important utilization in electronic and optoelectronic devices. The aim of this work is to study the effect of various substrates with metal or metal oxide layers including Au, Ag, Cu and Au+Cu alloy on the structural, morphological and optical properties of ZnO micro- and nanostructures. In addition, the relevant growth mechanisms are also proposed. The experiments are carried out in a quartz tube using a vapor phase transport of a carbon-zinc oxide mixture at different temperatures (900-1000˚C).

The main thesis work involves six distinct studies. Firstly, the conditions to grow ZnO micro- and nanostructures deposited on various substrates such as Si, GaN and corning glass without metal buffer layers are studied and optimum conditions for each morphology are identified. The results indicate that a gas pressure in range of 70 and 90 standard cubic centimeters per minute and 15 cm distance between the source and substrates are necessary for formation of nanostructures with diameters less than 100 nm. ZnO micro-sphere structure with a radius of around 1.5 µm was obtained under 80 standard cubic centimeters per minute (sccm) gas pressure rate and 30 cm distance from the source.

The multipods composed of nanowires and nanorods have been grown on different distributions of Ag nanoparticles on silicon substrates. A low distribution of Ag particles on the substates results in formation of multipod structure with pods ranged from 50-100 nm in diameter, and several micrometers in length. The diameters of the pods are increased (400 nm- 500 nm) while the substrate with more concentration of Ag particles is used.

ZnO flower-like multisheets were grown on silicon and corning glass substrates with Cu and Cu+Au alloy buffer layers. Comparison with the clean silicon substrate, the PL spectrum of the flower grown on the Cu/Si shows a higher intensity UV emission peak and the lower intensity visible emission peak. The spectrum also exhibits a higher intensity of the visible emission for ZnO crystalline on the Au+Cu/Si and Cu/Si than the ZnO grown on Si substrate. Shift of the E_2 mode in Raman spectrum indicates that the nanowires or nanosheets grown on metal buffer layers are under more in-plane stress.

ZnO peach-like morphology was grown on MgO (111) substrate with copper oxide buffer. The sizes of the peaches are not uniform and the diameters of the peaches are ranged from 2 to 5 micrometers. The photoluminescence spectrum demonstrates a strong peak in the ultraviolet (UV) region at around 380 nm, originated from the exciton related recombination. The peak positions at 495 and 520 nm can be assigned to oxygen and zinc vacancies, respectively. The high intensity of E_2 (high) mode in the Raman spectrum indicates a good crystallization of the prepared sample.

Two different quartz tubes were used to study the effect of different vapor super-saturation on the samples. The XRD patterns have indicated that the crystalline quality of the samples grown using one closed end tube was better than those with both opened ends. Based on the field emission scanning electron microscope images, larger ZnO nanostructures were obtained from one closed end tube due to the O_2-rich atmosphere.

Abstrak tesis yang dikemukan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SIFAT FIZIK DAN OPTIK ZINK OKSIDA MIKRO- DAN NANOSTRUKtUR DIENAPKAN PADA PELBAGAI SUBSTRAT

Oleh

AHMAD KAMALIANFAR

Januari 2014

Pengerusi : Profesor Abdul Halim Shaari, PhD
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Tesis ini bertujuan untuk mengkaji beberapa ciri yang tidak diketahui ke atas ZnO mikro dan nano sebagai salah satu bahan yang paling berpotensi dalam dekad ini. Selain itu, interaksi antara komponen-komponen yang terdiri daripada ZnO, lapisan penampan dan substrat boleh menghasilkan ciri-ciri fizik baru untuk beberapa penggunaan penting dalam alat elektronik dan optoelektronik. Tujuan utama kajian ini adalah untuk mengetahui kesan pelbagai substrat dengan logam atau logam lapisan oksida termasuk Au, Ag, Cu dan aloi Au-Cu pada sifat-sifat struktur, morfologi dan optik untuk mikro- dan nanostruktur ZnO. Di samping itu, mekanisme pertumbuhan yang berkaitan juga dicadangkan.

Eksperimen dijalankan dalam tiub kuarza dengan persekitaran fasa wap campuran oksida karbon-zink pada suhu yang berbeza (900-1000 ˚C).

Kerja-kerja tesis utama melibatkan enam kajian yang berbeza. Pertama, syarat-syarat untuk berkembang ZnO mikro dan nano disimpan pada pelbagai substrat seperti Si, GaN dan kaca corning tanpa lapisan penampan logam dikaji dan syarat-syarat yang optimum untuk setiap morfologi. Keputusan menunjukkan bahawa tekanan gas dalam lingkungan 70 dan 90 sentimeter padu per minit dan jarak 15 cm jarak antara sumber dan substrat diperlukan bagi pembentukan nano dengan diameter kurang daripada 100nm. ZnO struktur mikro sfera dengan jejari kira-kira 1.5 µm telah diperolehi di bawah 80 sccm kadar tekanan gas dan 30 cm jarak dari sumber.

Multipods yang terdiri daripada nanowayer dan nanorod telah ditanam ke atas nanopartikel Ag dengan taburan yang berbaza pada substrat silikon. Bagi substrat dengan taburan Ag yang rendah menghasilkan multipod nanowayer berdiameter antara 50-100 nm, dan beberapa mikrometer panjang. Diameter ranting meningkat (400 nm-500 nm) manakala substrat dengan kepekatan lebih daripada zarah Ag digunakan. Multi-lapisan ZnO bak-bunga

ditumbuhkan atas substrat silikon dan kaca corning dengan Cu dan aloi Cu+Au selagai lapisan penampan. Perbandingan dengan substrat silikon bersih, spektrum PL bagi bunga yang ditumbuh pada Cu/Si menunjukkan intensiti puncak pancaran UV yang lebih tinggi dan puncak pancaran berintensiti rendah. Spektrum juga mempamerkan intensiti pancaran boleh lihat yang lebih tinggi untuk kristal ZnO di atas Au+Cu/Si dan Cu/Si daripada ZnO tambuh diatas substrat Si. Peralihan mod E_2 dalam spektrum Raman menunjukkan bahawa nanowayer atau nanolapisan tumbuh di atas lapisan penampan logam adalah berada di bawah tekanan kedalam satah.

Pembentukan morfologi ZnO bak-peach ditumbuhkan di atas substrat MgO (111) dengan kuprum oksida sebagai penampan. Saiz "peach" adalah tidak seragam dan diameternya adalah antara 2 hingga 5 mikrometer. Spektrum PL menunjukkan puncak kukuh di rantau ultraungu (UV) pada sekitar 380 nm, berasal dari penggabungan semula eksiton. Kedudukan puncak pada 495 dan 520 nm masing-masing boleh diberikan kepada oksigen dan kekosongan zink. Keamatan tinggi E_2 mod (tinggi) dalam spektrum Raman menunjukkan penghabluran baik sampel dapat disediakan.

Dua tiub kuarza yang berbeza telah digunakan untuk mengkaji kesan yang berbeza wap super tepu ke atas sampel. Corak XRD telah menunjukkan bahawa kualiti kehabluran sampel ditumbuh menggunakan satu hujung tiub tertutup adalah lebih baik daripada kedua-dua hujung dibuka. Berdasarkan imej FESEM struktur nano ZnO lebih besar diperolehi daripada tiub separa tutup dengan lebihan O_2.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

CVD	Chemical vapor deposition
NP	Nanoparticle
NW	Nanowire
PL	Photoluminescence
PVD	Physical vapor deposition
Sccm	Standard cubic centimeters per minute
SEM	Scanning electron microscope
VLS	Vapor-liquid-solid
VPT	Vapor phase transport
VS	Vapor-solid
XRD	X-ray diffraction
UV-Vis	Ultraviolet–visible

CHAPTER 1

INTRODUCTION

The growth and characterization of micro- and nano-scale structures based on spontaneous formation provides a deeper understanding of functional materials and growth mechanisms for advanced applications. It was reported that by controlling the growth kinetics of the process in vapor phase transport method, a number of morphologies can be produced. During the past decades, a significant step after the growth of single component nanostructures is the synthesis of heterostructure nanocrystals of materials. The study of metal interfaces in metal-semiconductor heterostructure nanocrystal systems has been of great interest to improve the optical properties including luminescence intensity and enhance the efficiency of light-emitting materials (Biteen et at., 2005; Hsieh et al., 2007). Additionally, the interaction between the components can produce new physical properties which may be of great use in electronic and optoelectronic devices.

1.1 Back ground and scope of study

Much attention has focused on low dimensional semiconductor materials due to several applications of them in nano scale and high performance devices. Nanostructured based wide band gap semiconductors had always been an interesting classification of semiconductors because of extra ordinary properties in physical, chemical, electrical and optical fields. This has been evidenced by a number of publications in this field. Nanostructures commonly show the same crystal structures and lattice constants as their bulk while their physical, electrical and optical properties are different from their bulk counterpart.

Oxides of wide band gap semiconductors such as ZnO, SnO_2, TiO_2 and PbO_2 exhibit several kinds of nanostructures comprising nanowires, nanorods, nanosheets, nanohollows and nanobelts. Among them, a key technological material, ZnO will be focused in this study.

A versatile semiconductor material, Wurtzite ZnO has a wide direct band gap (Eg=3.37 eV) and high value exciton binding energy (~ 60 meV), making it a promising candidate for optoelectronic devices, UV lasers, and sensors (Kind et al., 2002; Jing et al., 2008). In addition to one dimensional ZnO structures, some novel nano- and micro-scale morphologies, such as sheets, plates, disks and flowers, in two or three dimensions are of interest for their high surface to volume ratio, nanometer scale thickness, excellent permeation, and distinct optical and photocatalytic activities for applications such as sensing (Wang at al., 2007; Ng et al., 2003; Pawar et al., 2012).

In other side, some metals transform to their oxide phase during experiment process due to the high temperature condition. Therefore, the integration of wurzite ZnO with metal oxide provides a heterojunction with the unique ferroelectric, ferromagnetic and sensing properties which has strong potential for applications in humidity sensor (Zainelabdin et al., 2012; Zhu et al., 2006).

Among all semiconductors, ZnO is one of the most semiconducting materials that is used in excess of 1.2 million tones around the world annually. Various properties of ZnO including chemical activity, UV absorption, white color and thermal conductivity cause diverse applications in enamel coatings, pigment in paints, photocopy, white ink, flame retardant, fungicides, cements, tire, glass and dental cements. Followed by the U.S, China is the dominant supplier and also largest users (Wayne, 2012).

The first performance of ZnO as metal-semiconductor returns to the 1920s. A contact between a thin copper wire and ZnO crystal provides current flow in only one direction. Using a radio circuit, the alternating current is converted to direct current (Jagadish and Pearton, 2006). Research and development efforts on ZnO synthesis and characterization have been underway as early as 1935. From about the 1960s on, growth and deposition of ZnO thin film has attracted much attention due to the immense applications in many optoelectronic devices such as sensors (Comini et al., 2002), solar cell and high frequency surface acoustic wave devices (Hickernell et al., 2000).

1.2 Problem statement and objectives

Hierarchically structure is a new class of materials with promising applications in many areas and is made by contacting oxide semiconductor-metal or ceramic-ceramic interface (Yousefi et al., 2010), as proposed by Nakamura et al. (1986). They can promote light utilization by absorption and reflection inside the material (Heinlaan et al., 2008).

To gain this goal, the surface can be modified by introducing a metal or metal oxide on the surface. Once light with wavelength larger than the particle size of a metal strikes to the surface of the metal, the resonance conditions cause the free electrons in the metal to oscillate. This is addressed to the surface plasmon resonance. Optical and morphological properties of ZnO micro and nanocomposites are important factors due to several applications of these composites in optoelectronic and sensing devices. Obtaining high quality heterostructures with improved optical properties is one of the biggest challenges in macro and nanostructures researches. It is known that, vapor phase transport method is a simple and cost-effective approach to growth ZnO micro- and nanostructures. Recently, use of noble metals (Au, Ag, Pt) as a component of composites can change the surface states resulting in higher optical and sensing properties (Huang et al. 2009). Although the noble metals such as gold and silver with wide surface plasmon and electron storage possession and also copper have been used to enhance charge separation in metal-semiconductor systems (Merga et al., 2008; Li et al., 2007), but some of their effects on the optical and morphological properties of ZnO micro- and nanostructures are not reported.

The main objectives of this thesis are:

1) To find optimum condition growing of ZnO micro- and nanostructures using a vapor phase transport method.
2) To grow and characterize structural, morphological and optical properties of ZnO micro- and nanostructures on pure and functional substrates with metals and metal oxide.
3) To propose some new growth mechanisms of ZnO micro- and nanostructures due to the influence of metals and metal oxides as functional surfaces.
4) To investigate of metal size and shape effects on the optical and morphological properties of ZnO micro- and nanostructures.
5) To study of vapor concentration effect on structural and optical properties of ZnO nanoscales.

1.3 Thesis overview

In this study, vapor phase synthesis and characterization of ZnO micro- and nanostructures on pure and functional surfaces were investigated. Vapor phase transport method was employed as growth technique. Chapter 2 includes background information on ZnO and fundamental properties of ZnO. Chapter 3 involves theoretical discussion about ZnO structure, optical characterization of semiconductors and study of semiconductor surface. The optical characterization comprises photoluminescence spectroscopy, Raman spectroscopy and ultraviolet-visible absorption. Two types of growth mechanisms of nanostructures, vapor-liquid-solid (VLS) growth and vapor-solid (VS) growth are discussed in chapter 3. In chapter 4, the experimental procedures including the preparation of the functional surfaces and growth of ZnO micro- and nanostructures on them are explained. Chapter 5 is divided into two parts. The first part demonstrates the results of products grown on the pure substrates and the second part shows the results of the ZnO structures grown on the functional surfaces with metal or metal oxides buffer layers. Chapter 6 provides the conclusion of the work as well as several suggestions for future works.

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