UNIVERSITI PUTRA MALAYSIA

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

AHMAD KAMALIANFAR

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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

PHYSICAL AND OPTICAL PROPERTIES OF ZINC OXIDE MICRO- AND NANOSTRUCTURES DEPOSITED ON VARIOUS SUBSTRATES

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January 2014

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
Fakulti : Sains

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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I certify that a Thesis Examination Committee has met on 20 January 2014 to conduct the final examination of Ahmad Kamalianfar on his thesis entitled "Physical and Optical Properties of Zinc Oxide Micro- and Nanostructures Deposited on Various Substrates" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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Universiti Putra Malaysia
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Sidek bin Hj Ab Aziz, PhD
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Universiti Putra Malaysia
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Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Arshad Saleem Bhatti, PhD
Professor
COMSATS Institute of Information Technology
Pakistan
(External Examiner)

NORITAH OMAR, PhD
Associate Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 17 February 2014

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:

Abdul Halim Shaari, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Lim Kean Pah, PhD
Assoc. Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Chen Soo Kien, PhD
Assoc. Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

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Signature: _____
Name of Member of Supervisory Committee: Assoc. Prof. Dr. Chen Soo Kien

Sigature: _____
Name of Member of Supervisory Committee: Assoc. Prof. Dr. Lim Kean Pah

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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.

REFERENCES

Alim, K. A., Fonoberov, V. A., and Balandin, A. A. (2005). Origin of the optical phonon frequency shifts in ZnO quantum dots. Applied Physics Letters, 86(5), 053103.

Alves, H., Pfisterer, D., Zeuner, A., Riemann, T., Christen, J., Hofmann, D. M. and Meyer, , B. K. (2003). Optical Material, Amsterdam, Neth. 23, 33.

Ardenne, M., Das, V. (1938). Elektronen- Rastermikroskop Praktische Ausfhrung, Technical Physics. 19: 407.

Ashkenov, N. , Mbenkum, B. N. and Bundesmann, C. (2003). Journal of Applied Physics 93, N11, 126 (2003).

Baruah, S., and Dutta, J. (2009). Effect of seeded substrates on hydrothermally grown ZnO nanorods. Journal of Sol-Gel Science and Technology, 50(3), 456-464.

Birman, J. L. (1959). Polarization of Fluorescence in CdS and ZnS Single Crystals. Physical Review Letters, 2(4), 157-159.

Biteen, J. S., Pacifici, D., Lewis, N. S., and Atwater, H. A. (2005). Enhanced Radiative Emission Rate and Quantum Efficiency in Coupled Silicon Nanocrystal-Nanostructured Gold Emitters. Nano Letters, 5(9), 1768-1773.

Burton, W. K., Cabrera, N., and Frank, F. C. (1951). The Growth of Crystals and the Equilibrium Structure of their Surfaces. Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences, 243(866), 299-358.

Butcher, K. S. A., Hirshy, H., Perks, R. M., Wintrebert-Fouquet, M., and Chen, P. P. T. (2006). Stoichiometry effects and the Moss–Burstein effect for InN. Physica Status Solidi (a), 203(1), 66-74.

Butkhuzi, T. V., Bureyev, A. V., Georgobiani, A. N., Kekelidze, N. P., and Khulordava, T. G. (1992). Optical and electrical properties of radical beam gettering epitaxy grown n- and p-type ZnO single crystals. Journal of Crystal Growth, 117(1–4), 366-369.

Bylander, E. G. (1978). Surface effects on the low-energy cathodoluminescence of zinc oxide. Journal of Applied Physics, 49(3), 1188-1195.

Cagin, E., Yang, J., Wang, W., Phillips, J. D., Hong, S. K., Lee, J. W., and Lee, J. Y. (2008). Growth and structural properties of m-plane ZnO on MgO (001) by molecular beam epitaxy. Applied Physics Letters, 92(23), 233505.

Calleja, J. M., and Cardona, M. (1977). Resonant Raman scattering in ZnO. Physical Review B, 16(8), 3753-3761.

Chang, P.-C., Fan, Z., Wang, D., Tseng, W.-Y., Chiou, W.-A., Hong, J., and Lu, J. G. (2004). ZnO Nanowires Synthesized by Vapor Trapping CVD Method. Chemistry of Materials, 16(24), 5133-5137.

Comini, E. (2006). Metal oxide nano-crystals for gas sensing. Analytica Chimica Acta, 568(1–2), 28-40.

Dalal, S. H., Baptista, D. L., Teo, K. B. K., Lacerda, R. G., Jefferson, D. A., and Milne, W. I. (2006). Controllable growth of vertically aligned zinc oxide nanowires using vapour deposition. Nanotechnology, 17(19), 4811.

Damen, T. C., Porto, S. P. S., and Tell, B. (1966). Raman Effect in Zinc Oxide. Physical Review, 142(2), 570-574.

Dingle, R. (1969). Luminescent Transitions Associated With Divalent Copper Impurities and the Green Emission from Semiconducting Zinc Oxide. Physical Review Letters, 23(11), 579-581.

Eberspacher, C., Fahrenbruch, A. L., and Bube, R. H. (1986). Properties of ZnO films deposited onto InP by spray pyrolysis. Thin Solid Films, 136(1), 1-10.

Emtage, P. R. (1977). The physics of zinc oxide varistors. Journal of Applied Physics, 48(10), 4372-4384.

Fonoberov, V. A., and Balandin, A. A. (2004). Origin of ultraviolet photoluminescence in ZnO quantum dots: Confined excitons versus surface-bound impurity exciton complexes. Applied Physics Letters, 85(24), 5971-5973.

Fowler, C. E., Khushalani, D., and Mann, S. (2001). Facile synthesis of hollow silica microspheres. Journal of Materials Chemistry, 11(8), 1968-1971.

Garces, N. Y., Wang, L., Bai, L., Giles, N. C., Halliburton, L. E., and Cantwell, G. (2002). Role of copper in the green luminescence from ZnO crystals. Applied Physics Letters, 81(4), 622-624.

Harrison, S.E., Conductivity and Hall e.ffect of ZnO at low temperatures, Physical Review 93 52 (1954) 52.

Haynes, J. R. (1966). Experimental Observation of the Excitonic Molecule. Physical Review Letters, 17(16), 860-862.

He, J. H., Ho, C. H., Wang, C. W., Ding, Y., Chen, L. J., and Wang, Z. L. (2008). Growth of Crossed ZnO Nanorod Networks Induced by Polar Substrate Surface. Crystal Growth and Design, 9(1), 17-19.

Heinlaan, M., Ivask, A., Blinova, I., Dubourguier, H. C., and Kahru, A. (2008). Toxicity of nanosized and bulk ZnO, CuO and TiO2 to bacteria Vibrio fischeri and crustaceans Daphnia magna and Thamnocephalus platyurus. Chemosphere, 71(7), 1308-1316.

Hejazi, S. R., Hosseini, H. R. M., and Ghamsari, M. S. (2008). The role of reactants and droplet interfaces on nucleation and growth of ZnO nanorods synthesized by vapor-liquid-solid (VLS) mechanism. Journal of Alloys and Compounds, 455(1-2), 353-357.

Hernadi, K., Fonseca A., Nagy, J. B., Bernaerts, D. and Lucas, A. A. (1996). Fe-catalyzed carbon nanotube formation. Carbon 34(10): 1249-1257.

Herring, C. (1951). Some Theorems on the Free Energies of Crystal Surfaces. Physical Review, 82(1), 87-93.

Hickernell, F. (2000). Thin-Films For Saw Devices. International Journal of High Speed Electronics and Systems 10(03): 603-652.

Hong, J., Kim, K., Heo, J., and Chung, I. Formation of square matrix pores on Al film utilizing focused ion beam milled indent. Thin Solid Films, 518(16), 4572-4577.

Hopfield, J. J., and Thomas, D. G. (1965). Polariton Absorption Lines. Physical Review Letters, 15(1), 22-25.

Hotovy, I., Pezoldt, J., Kadlecikova, M., Kups, T., Spiess, L., Breza, J., Rehacek, V. Structural characterization of sputtered indium oxide films deposited at room temperature. Thin Solid Films, 518(16), 4508-4511.

Hou, K., Li, C., Lei, W., Zhang, X., Yang, X., Qu, K.,Hsing-Hung, H., and Chung-Chih, W. (2007). Amorphous ZnO transparent thin-film transistors fabricated by fully lithographic and etching processes. Applied Physics Letters, 91(1), 013502-013503.

Hsueh, T.-J., Hsu, C.-L., Chang, S.-J., and Chen, I. C. (2007). Laterally grown ZnO nanowire ethanol gas sensors. Sensors and Actuators B: Chemical, 126(2), 473-477.

Hu, Y., Zhou, X., Han, Q., Cao, Q., and Huang, Y. (2003). Sensing properties of CuO–ZnO heterojunction gas sensors. Materials Science and Engineering: B, 99(1–3), 41-43.

Huang, F.-C., Chen, Y.-Y., and Wu, T.-T. (2009). A room temperature surface acoustic wave hydrogen sensor with Pt coated ZnO nanorods. Nanotechnology, 20(6), 065501.

Hümmer, K., and Gebhardt, P. (1978). Angular dependence of the reflection spectra and directional dispersion of the anisotropic exciton polaritons in ZnO. physica status solidi (b), 85(1), 271-282.

Ianno, N. J., McConville, L., Shaikh, N., Pittal, S., and Snyder, P. G. (1992). Characterization of pulsed laser deposited zinc oxide. Thin Solid Films, 220(1–2), 92-99.

Iijima, S. (1991). Helical microtubules of graphitic carbon. Nature, 354(6348), 56-58.

Iwanaga, H., Fujii, M., and Takeuchi, S. (1993). Growth model of tetrapod zinc oxide particles. Journal of Crystal Growth, 134(3-4), 275-280.

Jagadish, C. and Pearton, S., (2006), Zinc Oxide Bulk, Thin Films and Nanostructures: Processing, Properties, and Applications, Amsterdam, Elsevier.

Janotti, A., and Van de Walle, C. G. (2007). Native point defects in ZnO. Physical Review B, 76(16), 165202.

Jing, Z., and Zhan, J. (2008). Fabrication and Gas-Sensing Properties of Porous ZnO Nanoplates. Advanced Materials, 20(23), 4547-4551.

Jun, S. T., and Choi, G. M. (1994). CO gas-sensing properties of ZnO/CuO contact ceramics. Sensors and Actuators B: Chemical, 17(3), 175-178.

Kelly, K. L., Coronado, E., Zhao, L. L., and Schatz, G. C. (2002). The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. The Journal of Physical Chemistry B, 107(3), 668-677.

Kim, J., Kim, W., and Yong, K. (2012). CuO/ZnO Heterostructured Nanorods: Photochemical Synthesis and the Mechanism of H2S Gas Sensing. The Journal of Physical Chemistry C, 116(29), 15682-15691.

Kiomarsipour, N., and Shoja Razavi, R. (2012). Characterization and optical property of ZnO nano-, submicro- and microrods synthesized by hydrothermal method on a large-scale. Superlattices and Microstructures, (52,4).

Klason, P., Moe Børseth, T., Zhao, Q. X., Svensson, B. G., Kuznetsov, A. Y., Bergman, P. J., and Willander, M. (2008). Temperature dependence and decay times of

zinc and oxygen vacancy related photoluminescence bands in zinc oxide. Solid State Communications, 145(5–6), 321-326.

Klingshirn, C. (2007). ZnO: Material, Physics and Applications. ChemPhysChem, 8(6), 782-803.

Kohan, A. F., Ceder, G., Morgan, D., and Van de Walle, C. G. (2000). First-principles study of native point defects in ZnO. Physical Review B, 61(22), 15019-15027.

Kolanek, K., Tallarida, M., Karavaev, K., and Schmeisser, D. In situ studies of the atomic layer deposition of thin HfO_2 dielectrics by ultra high vacuum atomic force microscope. Thin Solid Films, 518(16), 4688-4691.

Kong, X. Y., and Wang, Z. L. (2003). Spontaneous Polarization-Induced Nanohelixes, Nanosprings, and Nanorings of Piezoelectric Nanobelts. Nano Letters, 3(12), 1625-1631.

Kong, Y. C., Yu, D. P., Zhang, B., Fang, W., and Feng, S. Q. (2001). Ultraviolet-emitting ZnO nanowires synthesized by a physical vapor deposition approach. Applied Physics Letters, 78(4), 407-409.

Kumar, R. T. R., McGlynn, E., Biswas, M., Saunders, R., Trolliard, G., Soulestin, B., Henry, M. O. (2008). Growth of ZnO nanostructures on Au-coated Si: Influence of growth temperature on growth mechanism and morphology. Journal of Applied Physics, 104(8), 084309.

Lin, B., Fu, Z., and Jia, Y. (2001). Green luminescent center in undoped zinc oxide films deposited on silicon substrates. Applied Physics Letters, 79(7), 943-945.

Look, D. C., Reynolds, D. C., Sizelove, J. R., Jones, R. L., Litton, C. W., Cantwell, G., and Harsch, W. C. (1998). Electrical properties of bulk ZnO. Solid State Communications, 105(6), 399-401.

Lu, W., Gao, S., and Wang, J. (2008). One-Pot Synthesis of Ag/ZnO Self-Assembled 3D Hollow Microspheres with Enhanced Photocatalytic Performance. The Journal of Physical Chemistry C, 112(43), 16792-16800.

Mang, A., Reimann, K., and Rübenacke, S. (1995). Band gaps, crystal-field splitting, spin-orbit coupling, and exciton binding energies in ZnO under hydrostatic pressure. Solid State Communications, 94(4), 251-254.

Mardare, D., Iacomi, F., Cornei, N., Girtan, M., and Luca, D. Undoped and Cr-doped TiO2 thin films obtained by spray pyrolysis. Thin Solid Films, 518(16), 4586-4589.

McCluskey, M. D., and Jokela, S. J. (2009). Defects in ZnO. Journal of Applied Physics, 106(7), 071101.

Mendelsberg, R. J., Kerler, M., Durbin, S. M., and Reeves, R. J. (2008). Photoluminescence behavior of ZnO nanorods produced by eclipse PLD from a Zn metal target. Superlattices and Microstructures, 43(5-6), 594-599.

Meyer, B. K., Alves, H., Hofmann, D. M., Kriegseis, W., Forster, D., Bertram, F., Rodina, A. V. (2004). Bound exciton and donor–acceptor pair recombinations in ZnO. Physica status solidi (b), 241(2), 231-260.

Meyer, B., and Marx, D. (2003). Density-functional study of the structure and stability of ZnO surfaces. Physical Review B, 67(3), 035403.

Milev, D. R., Atanasov, P. A., Dikovska, A. O., Dimitrov, I. G., Petrov, K. P., and Avdeev, G. V. Er3+,Yb3+:YVO4 waveguides deposited on amorphous SiO2 by PLD and UVPLD. Thin Solid Films, 518(16), 4726-4729.

Mishra, P., Yadav, R. S., and Pandey, A. C. Growth mechanism and photoluminescence property of flower-like ZnO nanostructures synthesized by starch-assisted sonochemical method. Ultrasonics Sonochemistry, 17(3), 560-565.

Moazzami, K., Murphy, T. E., Phillips, J. D., Cheung, M. C.-K., and Cartwright, A. N. (2006). Sub-bandgap photoconductivity in ZnO epilayers and extraction of trap density spectra. Semiconductor Science and Technology, 21(6), 717.

Modeshia, D. R., Dunnill, C. W., Suzuki, Y., Al-Ghamdi, A. A., El-Mossalamy, E. H., Obaid, A. Y., Parkin, I. P. (2012). Control of ZnO Nanostructures via Vapor Transport. Chemical Vapor Deposition, 18(10-12), 282-288.

Montenegro, D. N., Agouram, S., Martínez-Tomás, M. C., Llorens, C., Reig, C., and Muñoz-Sanjosé, V. (2010). Crystal growth of ZnO micro- and nanostructures by PVT on c-sapphire and amorphous quartz substrates. Physics Procedia, 8(0), 121-125.

Mukae, K., Tsuda, K., and Nagasawa, I. (1979). Capacitance-vs-voltage characteristics of ZnO varistors. Journal of Applied Physics, 50(6), 4475-4476.

Muth, J. F. , Kolbas, R. M. , Sharma, A. K., Oktyabrsky, S. and Narayan, J., J. Appl. Phys. 85, 7884 (1999).

Naas, A., De Sousa-Meneses, D., Hakim, B., Regula, G., Beaufort, M. F., Belaidi, A., and Ntsoenzok, E. Optical and nuclear characterization of Xe-induced nanoporosity in SiO2. Thin Solid Films, 518(16), 4721-4725.

Nagar, S., and Chakrabarti, S. Evidence of p-doping in ZnO films deposited on GaAs. Thin Solid Films, 518(16), 4542-4545.

Nakamura, Y., Ando, A., Tsurutani, T., Okada, O., Miyayama, M., Koumoto, K., and Yanagida, H. (1986). GAS SENSITIVITY OF CuO/ZnO HETERO-CONTACT. Chemistry Letters, 15(3), 413-416.

Nanev, C. R., and Iwanov, D. (1982). Morphological Stability of Vapour Grown Metal Single Crystals. Crystal Research and Technology, 17(5), 575-584.

Ok, J. G., Tawfick, S. H., Juggernauth, K. A. , Sun, K. , Zhang, Y. and Hart, A. J. (2010). Electrically Addressable Hybrid Architectures of Zinc Oxide Nanowires Grown on Aligned Carbon Nanotubes. Advanced Functional Materials 20(15): 2470-2480.

Ozgur, U., Alivov, Y. I., Liu, C., Teke, A., Reshchikov, M. A., Dogan, S., Morkoc, H. (2005). A comprehensive review of ZnO materials and devices. Journal of Applied Physics, 98(4), 041301.

Pan, Z. W., Dai, Z. R., and Wang, Z. L. (2001). Nanobelts of Semiconducting Oxides. Science, 291(5510), 1947-1949.

Park, Y. S., Litton, C. W., Collins, T. C., and Reynolds, D. C. (1966). Exciton Spectrum of ZnO. Physical Review, 143(2), 512-519.

Partington, J.R. (1989). A short history of chemistry, 3rd Edition, Dover., Pawar, R. C., Shaikh, J. S. , Suryavanshi, S. S. and Patil, P. S. (2012). Growth of ZnO nanodisk, nanospindles and nanoflowers for gas sensor: pH dependency. Current Applied Physics. 12: 778-783.

Pawar, R. C., Shaikh, J. S., Suryavanshi, S. S., and Patil, P. S. (2012). Growth of ZnO nanodisk, nanospindles and nanoflowers for gas sensor: pH dependency. Current Applied Physics, (12, 3).

Pearton, S. J., and Jagadish, C. (2006). Zinc Oxide Bulk, Thin Films and Nanostructures: Processing, Properties, and Applications: Elsevier Science.

Pierson, H. O. (1992). Handbook of Chemical Vapor Deposition, Noyes Publications, Park Ridge.

Preethi, V., and Kanmani, S. (2013). Photocatalytic hydrogen production. Materials Science in Semiconductor Processing, 16(3), 561-575.

Raether, H. (1988). Surface plasmons on smooth surfaces Surface Plasmons on Smooth and Rough Surfaces and on Gratings (Vol. 111, pp. 4-39). Berlin: Springer Berlin Heidelberg.

Reynolds, D. C., Look, D. C., Jogai, B., Litton, C. W., Cantwell, G., and Harsch, W. C. (1999). Valence-band ordering in ZnO. Physical Review B, 60(4), 2340-2344.

Sa'aedi, A., Yousefi, R., Jamali-Sheini, F., Cheraghizade, M., Zak, A. K., and Huang, N. M. (2014). Optical properties of group-I-doped ZnO nanowires. Ceramics International, 40(3), 4327-4332.

Sarikov, A., Stegemann, B., and Schmidt, M. A model of the passivation of ultrathin SiO2 layer/Si substrate interfaces by atomic hydrogen from a thermalised plasma source. Thin Solid Films, 518(16), 4662-4666.

Saunders, R. B., McGlynn, E., Biswas, M. and Henry, M. O. (2010). Thermodynamic aspects of the gas atmosphere and growth mechanism in carbothermal vapour phase transport synthesis of ZnO nanostructures. Thin Solid Films 518(16): 4578-4581.

Scott, J. F. (1970). uv Resonant Raman Scattering in ZnO. Physical Review B, 2(4), 1209-1211.

Shan, G., Xu, L., Wang, G., and Liu, Y. (2007). Enhanced Raman Scattering of ZnO Quantum Dots on Silver Colloids. The Journal of Physical Chemistry C, 111(8), 3290-3293.

Silverstein, R. M., Bassler, C.G., Morrill, T.C., (1981). Spectrometric identification of organic compounds. New York: Wiley.

Sohma, M., Kawaguchi, K., and Fujii, Y. (1994). Structural characterization of a CuO/MgO artificially superstructured film by the x-ray diffraction method. Journal of Applied Physics, 75(4), 1952-1955.

Sun, X. W., and Kwok, H. S. (1999). Optical properties of epitaxially grown zinc oxide films on sapphire by pulsed laser deposition. Journal of Applied Physics, 86(1), 408-411.

Teke, A., Ã–zg, Ã., DoÄŸan, S., Gu, X., MorkoÃ§, H., Nemeth, B., Everitt, H. O. (2004). Excitonic fine structure and recombination dynamics in single-crystalline ZnO. Physical Review B, 70(19), 195207.

Thomas, D. G. (1960). The exciton spectrum of zinc oxide. Journal of Physics and Chemistry of Solids, 15(1–2), 86-96.

Valeur, B., and Berberan-Santos, M. r. N. (2011). A Brief History of Fluorescence and Phosphorescence before the Emergence of Quantum Theory. Journal of Chemical Education, 88(6), 731-738.

Vanheusden, K., Warren, W. L., Seager, C. H., Tallant, D. R., Voigt, J. A., and Gnade, B. E. (1996). Mechanisms behind green photoluminescence in ZnO phosphor powders. Journal of Applied Physics, 79(10), 7983-7990.

Ventura, J., Fina, I., Ferrater, C., Langenberg, E., Coy, L. E., Polo, M. C., Varela, M. Structural and dielectric properties of (001) and (111)-oriented BaZr0.2Ti0.8O3 epitaxial thin films. Thin Solid Films, 518(16), 4692-4695.

Voss, T., Bekeny, C., Wischmeier, L., Gafsi, H., Borner, S., Schade, W., Waag, A. (2006). Influence of exciton-phonon coupling on the energy position of the near-band-edge photoluminescence of ZnO nanowires. Applied Physics Letters, 89(18), 182107.

Wagner, R. S., and Ellis, W. C. (1964). Vapor-Liquid-Solid Mechanism of Single Crystal Growth. Applied Physics Letters, 4(5), 89-90.

Walle, V, C. G. (2000). Hydrogen as a Cause of Doping in Zinc Oxide. Physical Review Letters 85(5): 1012-1015.

Wang, X., Li, Q., Liu, Z., Zhang, J., Liu, Z., and Wang, R. (2004). Low-temperature growth and properties of ZnO nanowires. Applied Physics Letters, 84(24), 4941-4943.

Wang, H. T., Kang, B. S., Ren, F., Tien, L. C., Sadik, P. W., Norton, D. P., Lin, J. (2005). Hydrogen-selective sensing at room temperature with ZnO nanorods. Applied Physics Letters, 86(24), 243503.

Wang, J., Sallet, V., Jomard, F., Botelho do Rego, A. M., Elamurugu, E., Martins, R., and Fortunato, E. (2007). Influence of the reactive N2 gas flow on the properties of rf-sputtered ZnO thin films. Thin Solid Films, 515(24), 8780-8784.

Waterhouse, G. I. N., Bowmaker, G. A., and Metson, J. B. (2001). Oxidation of a polycrystalline silver foil by reaction with ozone. Applied Surface Science, 183(3-4), 191-204.

Wayne, M. M., 2012, China's Rare Earth Industry and Export Regime: Economic and Trade Implications for the United States .

Williams, E. W. and H. B. Bebb, Edited by R. K. Willardson and A. C. Beer, (1972). Academic, New York.

Wu, Y., and Yang, P. (2001). Direct Observation of Vapor-Liquid-Solid Nanowire Growth. Journal of the American Chemical Society, 123(13), 3165-3166.

Xu, S., Wei, Y., Kirkham, M., Liu, J., Mai, W., Davidovic, D., Wang, Z. L. (2008). Patterned Growth of Vertically Aligned ZnO Nanowire Arrays on Inorganic

Substrates at Low Temperature without Catalyst. Journal of the American Chemical Society, 130(45), 14958-14959.

Yang, X., Du, G., Wang, X., Wang, J., Liu, B., Zhang, Y., Yang, S. (2003). Effect of post-thermal annealing on properties of ZnO thin film grown on c-Al2O3 by metal-organic chemical vapor deposition. Journal of Crystal Growth, 252(1–3), 275-278.

Yao, B. D., Chan, Y. F., and Wang, N. (2002). Formation of ZnO nanostructures by a simple way of thermal evaporation. Applied Physics Letters, 81(4), 757-759.

Ye, C., Fang, X., Hao, Y., Teng, X., and Zhang, L. (2005). Zinc Oxide Nanostructures: Morphology Derivation and Evolution. The Journal of Physical Chemistry B, 109(42), 19758-19765.

Yearian, H.J., (1935). Intensity of di.raction of electrons by ZnO, Physical Review 48, 631 (1935).

Yi, G.-C., and Choi, H.-J. (2012). Vapor-Liquid-Solid Growth of Semiconductor Nanowires Semiconductor Nanostructures for Optoelectronic Devices (pp. 1-36): Springer Berlin Heidelberg.

Yin, X., Que, W., Fei, D., Shen, F., and Guo, Q. (2012). Ag nanoparticle/ZnO nanorods nanocomposites derived by a seed-mediated method and their photocatalytic properties. Journal of Alloys and Compounds, 524(0), 13-21.

Yousefi, R., and Kamaluddin, B. (2009). Dependence of photoluminescence peaks and ZnO nanowires diameter grown on silicon substrates at different temperatures and orientations. Journal of Alloys and Compounds, 479(1-2), L11-L14.

Yousefi, R., Muhamad, M. R., and Zak, A. K. (2010). Investigation of indium oxide as a self-catalyst in ZnO/ZnInO heterostructure nanowires growth. Thin Solid Films, 518(21), 5971-5977.

Yu, P. and Cardona, M. (1990). Fundamentals of Semiconductors: Physics and Material Properties, 2nd ed. Springer-Verlag, Berlin.

Zainelabdin, A., Amin, G., Zaman, S., Nur, O., Lu, J., Hultman, L., and Willander, M. (2012). CuO/ZnO Nanocorals synthesis via hydrothermal technique: growth mechanism and their application as Humidity Sensor. Journal of Materials Chemistry, 22(23), 11583-11590.

Zeng, H., W. Cai, J. Hu, G. Duan, P. Liu and Y. Li (2006). Violet photoluminescence from shell layer of Zn/ZnO core-shell nanoparticles induced by laser ablation. Applied Physics Letters 88(17): 171910.

Zeng, H., W. Cai, Y. Li, J. Hu and P. Liu (2005). Composition/Structural Evolution and Optical Properties of ZnO/Zn Nanoparticles by Laser Ablation in Liquid Media. The Journal of Physical Chemistry B 109(39): 18260-18266.

Zhang, Q., and Cao, G. (2001). Nanostructured photoelectrodes for dye-sensitized solar cells. Nano Today, 6(1), 91-109.

Zhang, Y., Wang, N. (2002). A Simple Method To Synthesize Nanowires. Chemistry of Materials 14(8): 3564-3568.

Zhu, Y., Sow, C. H., Yu, T., Zhao, Q., Li, P., Shen, Z., Thong, J. T. L. (2006). Co-synthesis of ZnO–CuO Nanostructures by Directly Heating Brass in Air. Advanced Functional Materials, 16(18), 2415-2422.

Zhu, Z., Chen, T.-L., Gu, Y., Warren, J., and Osgood, R. M. (2005). Zinc Oxide Nanowires Grown by Vapor-Phase Transport Using Selected Metal Catalysts: A Comparative Study. Chemistry of Materials, 17(16), 4227-4234.