

Table of contents

Chapter 1: Introduction	1
1.1. Background and scope of study	1
1.2. Aim and objectives.....	5
1.3. Thesis structure	6
Chapter 2: Literature Review	8
2.1. Introduction to one-dimensional ZnO nanostructures	8
2.1.1. Discovery of ZnO nanobelts (2001).....	8
2.1.2. Growth of aligned ZnO nanowires (2004—2005).....	10
2.1.3. Doping of ZnO nanostructures.....	11
2.2. Fundamental properties and theoretical models.....	14
2.2.1. Crystal structure of ZnO	15
2.2.2. Optical properties	17
2.2.2.1. Band-gap engineering of ZnO.....	17
2.2.2.2. Burstein-Moss effect	18
2.2.3. Photoluminescence.....	19
2.2.3.1. Surface effects on photoluminescence properties	23
2.2.4. Vibrational properties and Raman spectroscopy	25
2.2.5. Field Electron Emission	28
2.2.5.1. Fowler-Nordheim Plot (F-N Plot).....	29
Chapter 3: Experimental methods and instrumentation	31
3.1. Thermal evaporation method.....	31
3.1.1. Conventional thermal evaporation set-up	32
3.1.2. Modification of thermal evaporation set-up.....	34
3.2. Epitaxial growth of nanostructures	35
3.2.1. Vapor-Liquid-Solid (VLS) method.....	36
3.2.2. Vapor-Solid (VS) method	43
3.2.3. Different morphologies of 1D ZnO nanostructures	43
3.3. Instrumentation	45
3.3.1. Field Emission Scanning Electron Microscope (FESEM) and Energy Dispersive X-Ray (EDX)	46

3.3.2. Transmission Electron Microscope (TEM) and Select Area Electron Diffraction (SAED).....	47
3.3.3. X-Ray Diffraction (XRD)	49
3.3.4. Auger electron spectroscopy (AES).....	50
3.3.5. Photoluminescence and Raman spectroscopies	52
3.3.6. Field emission measurements	53
 Chapter 4: Fabrication and characterization of un-doped ZnO nanowires.....	57
4.1. Introduction	57
4.2. Experimental details.....	58
4.3. Growth and characterization of ZnO nanowires using a conventional thermal evaporation set-up	59
4.4. Growth and characterization of ZnO nanowires using a modified thermal evaporation set-up	66
4.4.1.Source temperature effect on morphological properties of ZnO nanowires grown using a modified thermal evaporation set-up	75
 Chapter 5: Fabrication and characterization of doped-ZnO nanowires	80
5.1. Introduction	80
5.2. Growth and characterization of $ZnO_xMg_{1-x}O$ nanowires	80
5.2.1. Growth of $Zn_xMg_{1-x}O$ nanowires using a conventional set-up	81
5.2.1.1. Experimental details.....	81
5.2.1.2. Results and discussion	81
5.2.2. Growth of $Zn_xMg_{1-x}O$ nanowires using a modified set-up	90
5.2.2.1. Experimental details.....	90
5.2.2.2. Results and discussion	91
5.2.3. Field emission study of $Zn_{1-x}Mg_xO$ nanowires	101
5.3. Al-doped ZnO nanowires using AlN thin films	105
5.3.1. Experimental details.....	105
5.3.2. Results and discussion	105
5.4. Growth of ZnO/ZnInO heterostructure nanowires	112
5.4.1. Experimental details.....	112
5.4.2. Results and discussion	113
 Chapter 6: Growth and doping of ZnO nanobelts	126

6.1. Introduction.....	126
6.2. S- and Sn-doped ZnO nanobelts.....	126
6.2.1. Experimental details.....	126
6.2.2. Results and discussion	127
6.3. The effects of annealing temperature on structural and optical properties of S-doped ZnO nanobelts	136
Chapter 7: Conclusions.....	141
Appendix A	144
A.1. List of Publication.....	144
A.2. Internationl Conference Attendent.....	145
Bibliography.....	146

List of Figures

Figure 1. 1. Worldwide ZnO consumption per continent.....	2
Figure 1.2. Publication statistics on nanostructures for ZnO. The data were received on May 20, 2009 through the Institute of Scientific Information (ISI) database using the following key words that appear in the title, abstracts, and keywords: ZnO (or zinc oxide) together with nanowire, nanobelt, nanorod, nanoribbon, nanotip, nanofiber, nanoring, nanohelix, nanospring, nanobrush, or nanoflower.....	3
Figure 1.3. A summary of ZnO applications and properties.....	4
Figure 1.4. The map of physics adopted from Physics World.....	5
Figure 2.1. TEM images of the as-synthesized ZnO nanobelts	8
Figure 2.2. SEM images of (a) single-crystal nanospring, (b) nanoring, and (c) superlattice structured nanohelix of ZnO.....	9
Figure 2.3. Aligned ZnO nanowire arrays that were grown on a sapphire surface.....	10
Figure 2.4. Stick and ball representation of ZnO crystal structures: (a) cubic rocksalt (B_1) , (b) cubic zinc blende (B_3), and (c) hexagonal wurtzite (B_4). The shaded gray and black spheres denote Zn and O atoms, respectively	16
Figure 2.5. The hexagonal wurtzite structure of ZnO.....	16
Figure 2.6. Schematic of the band-gap in (a) a pure state and (b) a doped state.....	19
Figure 2.7. Schematic of the typical PL process.....	20
Figure 2.8. Radiative recombination process: (a) band to band, (b) donor to valance band, (c) conduction band to acceptor, (d) donor to acceptor, and (e) non-radiative process via an intermediate state.	21
Figure 2.9. Schematic band diagram of DLEs in ZnO nanostructures based on the full potential linear muffin-tin orbital method and reported data.....	21
Figure 2.10. Schematic of the three visible emission processes, which show energy levels of O vacancy in ZnO structure.....	23
Figure 2.11. First Brillouin zone (BZ) of the wurtzite structure	26
Figure 2.12. Schematic representation of the atomic displacement of the BZ optical modes in a hexagonal lattice.....	27

Figure 2.13. Schematic diagram of different scatterings: (a) Rayleigh scattering, (b) Stokes Raman scattering, and (c) Anti-Stokes Raman scattering. The v_i and v_f indicate the initial and final states.....	27
Figure 3.1. Photographs of the experimental set-up from different points-of-view, including the thermal evaporation system and two mass flow meters, which control gas flow during the experiment based on sccm (standard cubic centimeters per minute), as well as a temperature calibration diagram.....	32
Figure 3.2. Schematic of the thermal evaporate deposition system for the synthesis of 1D nanostructures.....	32
Figure 3.3. Schematic of the modified set-up used for the growth of ZnO nanowires.....	34
Figure 3.4. Schematic illustration of the growth mechanism of Si nanowires.....	36
Figure 3.5. Sputtering system (model SPI) that was used in our lab for producing a gold coating on Si wafers.....	37
Figure 3.6. FESEM and AFM images of 30 s Au sputtered on a Si (111) substrate after 30 min of thermal annealing at 700 °C.....	38
Figure 3.7. ZnO nanowires grown using the VLS method. Au droplets at the tips of these nanowires can be clearly observed.....	39
Figure 3.8. Au-Zn phase diagram.....	40
Figure 3.9. Schematic of ZnO nanowire formation by the VLS process.....	41
Figure 3.10. A model of ZnO nanowires growth by the VLS method: (a) schematic of the oxidation of Zn islands and nucleation of ZnO at the liquid-solid interface and (b) oxidation of a Zn island through nanorods	42
Figure 3.11. Typical growth morphologies of 1D ZnO nanostructures and the corresponding facets.....	44
Figure 3.12. (a) ZnO nanostructures that were grown using the VS method: (a) ZnO nanowires (b) ZnO nanobelts and dual-nanorings.....	45
Figure 3.13. A photograph of the FEI Quanta 200F FESEM with EDX set-up	47
Figure 3.14. A photograph of the TEM microscopy unit (Philips CM200).....	48
Figure 3.15. Schematic of the diffraction of an X-rays beam by parallel atomic planes in a crystalline material.....	49

Figure 3.16. Basic features of a typical XRD experiment as well as the Siemens D5000 set-up.....	50
Figure 3.17. Schematic of a generated Auger electron emission.....	51
Figure 3.18. AES, JAMP-9500F set-up in our lab as well as schematic of all process in Auger spectrometer	52
Figure 3.19. PL and Raman spectrometers set-up, model: Jobin Yvon Horiba HR 800 UV.	53
Figure 3.20. (a) Instrument used for field electron emission studies, (b) Schematic diagram of the planar diode configuration assembly.....	54
Figure 4.1. FESEM images of the ZnO nanowires grown on Si(111) at different temperatures : (a) 700 °C, (b) 550 °C, and (c) 400 °C	59
Figure 4.2. FESEM images of the ZnO nanowires grown on Si(100) at different temperatures : (a) 700 °C, (b) 550 °C, and (c) 400 °C	60
Figure 4.3. (a) XRD patterns of the ZnO nanowires grown on Si(111) at different temperatures. (b) XRD patterns of the ZnO nanowires grown on Si(100) at different temperatures.....	61
Figure 4.4. PL spectra of the ZnO nanowires grown on Si(111) at (a ₁) 700 °C, (b ₁) 550 °C, (c ₁) 400 °C and on Si(100) at (a ₂) 700 °C, (b ₂) 550 °C, and (c ₂) 400 °C.....	62
Figure 4.5. UV emission spectra for various nanowires diameters. A blue-shift from 381 to 375 nm in the peak position of the UV emission is clearly visible as the nanowires diameter decreases.....	64
Figure 4.6. Peak intensities of the UV and DLE emission are plotted against the nanowires aspect ratios. The UV emission was more intense in nanowires with small aspect ratios, while the DLE emission dominated in large aspect ratio nanowires.....	65
Figure 4.7. (a ₁) and (a ₂): Low- and high-magnification FESEM images of ZnO nanowires grown at 650 °C, respectively. (b ₁) and (b ₂): Low- and high-magnification FESEM images of ZnO nanowires grown at 600 °C, respectively. (c ₁) and (c ₂): Low- and high-magnification FESEM images of ZnO microdiscs grown at 550 °C, respectively.....	66
Figure 4.8. Schematic of nanostructures formation along the tube furnace.....	68
Figure 4.9. The green arrows show the diffusion of N ₂ gas along the one-ended tube, starting at the edge of the tube. In addition, the size of the green arrows shows the decrease in N ₂ gas diffusion along the tube, from the edge to the end of the tube that was placed at the center of the furnace.....	69

Figure 4.10. XRD patterns for the ZnO nanowires and microdiscs that were grown in different temperatures regions: (a) 650 °C, (b) 600 °C, and (c) 550 °C	70
Figure 4.11. Room temperature PL spectra of the ZnO nanowires and microdiscs that were grown at different temperatures: (a) 650 °C, (b) 600 °C, and (c) 550 °C.....	71
Figure 4.12. PL spectra of the ZnO nanowires that were grown in the two types of set-up.....	72
Figure 4.13. Raman spectra of the ZnO nanowires and microdiscs that were grown at different temperatures: (a) 650 °C, (b) 600 °C, and (c) 550 °C.....	74
Figure 4.14. (a) FESEM image of ZnO nanowires with hexagonal shapes that were grown at a source temperature of 950 °C. (b) FESEM image of ZnO nanowires with spear shapes that were grown at a source temperature of 1050 °C.....	75
Figure 4.15. (a) (a) High magnification FESEM image of ZnO nanospears. (b) TEM image of a single nanospear. (c) HRTEM image of a single nanospear. (d) SAED pattern of a single nanospear.....	76
Figure 4.16. XRD patterns of the hexagonal nanowires and nanospears.....	78
Figure 4.17. PL spectra of the hexagonal nanowires and nanospears. These spectra show demonstrate that the nanospears have lower optical properties than for the hexagonal nanowires.....	78
Figure 4.18. Raman spectra of the hexagonal nanowires and nanospears. These spectra show that nanospears have a lower crystallinity than for the hexagonal nanowires	79
Figure 5.1. XRD pattern of the source material before evaporation. The observed diffraction peaks are quite similar to those of single-crystalline wurtzite hexagonal bulk ZnO, except for the two peaks at 42.80° and 62.15° that belong to the cubic phase of $Zn_xMg_{1-x}O$	82
Figure 5.2. (a) FESEM image of the nanorods grown at 700 °C. (b) EDX spectrum of the top view of nanorods grown at 700 °C. (c) EDX spectrum and FESEM image of a single $Zn_xMg_{1-x}O$ nanowire with cubic shape. (d) EDX spectrum and FESEM image of a cross-sectional view of ZnO and $Zn_xMg_{1-x}O$ nanorods grown on a thin $Zn_{1-x}Mg_xO$ buffer layer deposited on a Si substrate at 700 °C.....	83
Figure 5.3. (a) FESEM image of nanosheets and nanorods grown at 800 °C. (b) EDX spectrum of the top view of the nanosheets and nanorods grown at 800 °C. (c) EDX and FESEM of the cross-sectional view of the ZnO nanosheets and nanorods grown on a Si substrate at 800 °C	84

Figure 5.4. (a) XRD pattern of ZnO nanorods deposited at 700 °C. (b) XRD pattern of ZnO nanosheets grown on the Si at 800 °C. This pattern shows an additional peak of ZnO in comparison to the other sample at 66.3 (200).....	85
Figure 5.5. Thin $Zn_{1-x}Mg_xO$ buffer layer and the ZnO nanostructure growth process mechanism on Si substrates. This pattern shows two different roles of Au during the formation of the nanostructures	87
Figure 5.6. PL spectra of the ZnO nanorods and nanosheets. The inset shows that the UV peak of the nanorods grown at 700 °C is blue-shifted.....	89
Figure 5.7. Schematic of set-up that used for growth of $Zn_{1-x}Mg_xO$ nanowires	91
Figure 5.8. Low-magnification FESEM images of the $Zn_{1-x}Mg_xO$ nanowires that were grown on the (a ₁) catalyst-free substrate, (b ₁) substrate coated with 10-nm-thick Au film, and (c ₁) substrate coated with 30-nm-thick Au film. (a ₂ -c ₂) High-magnification FESEM images of the $Zn_{1-x}Mg_xO$ nanowires with EDX spectra at different locations of along individual nanowires.....	92
Figure 5.9. FESEM image and EDX spectrum of the un-doped ZnO nanowires that grown on the catalyst-free substrate.....	95
Figure 5.10. Schematic of $Zn_{1-x}Mg_xO$ and ZnO nanowires formation on various substrates	96
Figure 5.11. XRD patterns of the $Zn_{1-x}Mg_xO$ nanowires grown on the (a) catalyst-free substrate, (b) substrate coated with 10-nm-thick Au film, (c) substrate coated with 30-nm-thick Au film, and (d) un-doped ZnO nanowires. No peaks from impurities are detected, except for sample (c), which shows an additional peak that corresponds to the Au(111) catalyst. The inset shows the shifts of (002) peaks of the $Zn_{1-x}Mg_xO$ nanowires in comparison to the (002) peak of the un-doped ZnO nanowires.....	98
Figure 5.12. PL spectra of the $Zn_{1-x}Mg_xO$ nanowires grown on the (a) catalyst-free substrate, (b) substrate coated with 10-nm-thick Au film, (c) substrate coated with 30-nm-thick Au film, and (d) un-doped ZnO nanowires. All of the $Zn_{1-x}Mg_xO$ samples show an obvious blue-shift in the UV emission in comparison to the un-doped ZnO nanowires.....	99
Figure 5.13. Raman spectra of the $Zn_{1-x}Mg_xO$ nanowires grown on the (a) catalyst-free substrate, (b) substrate coated with 10-nm-thick Au film, (c) substrate coated with 30-nm-thick Au film, and (d) un-doped ZnO nanowires. All of the nanowires show a sharp, strong and dominant peak at 437 cm^{-1} corresponding to the E ₂ (high) mode of the Raman active mode.....	100
Figure 5.14. (a) J-E plots of the field emission from the $Zn_{1-x}Mg_xO$ nanowires grown on the substrate coated with 10-nm-thick Au film (sample (a)) and substrate coated with 30-nm-thick Au film (sample (b)). (b) F-N plots of the field emission from these nanowires.....	102

Figure 5.15. I-t plots recorded of the $Zn_{1-x}Mg_xO$ nanowires grown on the: (a) substrate coated with 10-nm-thick Au film (sample (a)), and (b) substrate coated with 30-nm-thick Au film (sample (b)). The insets are the corresponding luminescence images of the nanowires.....	103
Figure 5.16. XRD pattern of AlN thin film with cubic structure deposited on glass	106
Figure 5.17. FESEM images and EDX spectra of the ZnO nanowires grown on the AlN thin film at (a) 600 °C and (b) 500 °C. The shapes of the ZnO nanowires are varied with the distance from the source material to the substrates.....	106
Figure 5.18. XRD patterns of the ZnO nanowires deposited at (a) 600 °C and (b) 500 °C. XRD pattern of the nanowires grown at 600 °C not only shows ZnO peaks but also presents three peaks at 38.45°, 44.65° and 48.80° which belong to ZnAlO composite.....	107
Figure 5.19. High resolution N (E) Auger electron emission spectroscopy of the ZnO nanowires deposited on the AlN thin film at 600 and 500 °C. (a) O spectra and (b) Zn spectra. These spectra show clearly a significant shift to higher energies for oxygen and zinc peaks for nanowires grown at 600 °C and also (c) Al spectra that show Al peaks only for the sample grown at 600 °C.....	108
Figure 5.20. Auger spectrum and FESEM image of ZnO nanowires grown on Si substrate that average diameter of these nanowires is about 60 nm	109
Figure 5.21. PL spectra of the ZnO nanowires deposited at 600 and 500 °C. The inset shows the UV peak of nanowires grown in the low temperature zone is blue shifted, because the diameters of nanowires in this zone are smaller than those grown in the high temperature zone.....	111
Figure 5.22. (a ₁) Low-magnification FESEM image and EDX spectrum for ZnO/ZnInO heterostructure nanowires grown for 90 min. (a ₂) High-magnification of a single ZnO/ZnInO heterostructure nanowire grown for 90 min. The black arrow shows that the growth direction of the nanowire is [0001]	113
Figure 5.23. (a ₁) A single ZnO/ZnInO heterostructure nanowire grown for 90 min with four spectra taken of four distinct regions along this nanowire: (A) of the tip, (B) of the upper half, (C) of the middle, and (D) of the bottom half regions of the nanowire	114
Figure 5.24. Low resolution FESEM image and EDX spectrum of the ZnO/ZnInO heterostructure nanowires grown for 50 min.....	115

Figure 5.25. A high-magnification FESEM image of a single ZnO/ZnInO heterostructure nanowire grown for 50 min, with three spectra taken of three regions along the nanowire: (A) of the tip, (B) of the middle, and (C) of the bottom half regions of the nanowire. These spectra indicate that indium is not detected in the bottom half region of the nanowire.....116

Figure 5.26. High resolution N (E) Auger electron emission spectroscopy of ZnO/ZnInO heterostructure nanowires grown for 90 min, obtained from two different regions (upper and bottom half) of a single nanowire. (a) Indium spectra corresponding to the MNN Auger electron emission from indium. These spectra show that the indium element is only detectable in the upper half part of the nanowire. (b) Oxygen spectra corresponding to the KLL Auger electron emission from oxygen. (c) Zinc spectra corresponding to the LMM Auger electron emission from zinc.....117

Figure 5.27. FESEM image of un-doped ZnO nanowires grown under the same conditions as the ZnO/ZnInO heterostructure nanowires. The inset shows some nanowires with smooth surfaces and without any metal at the nanowire tips.....118

Figure 5.28. XRD pattern of the source material before evaporation119

Figure 5.29. EDX results of materials remining in the boat after 30, 50, and 90 min of evaporation. This pattern shows that the content of carbon has decreased after 30 min dramatically. Also, it shows carbon act in evaporation of ZnO.....120

Figure 5.30. An FESEM image and EDX spectrum of the first deposition observed at 30 min121

Figure 5.31. Schematic illustrating the formation of ZnO/ZnInO heterostructure nanowires and the diffusion of self-catalyst of $\text{In}_{2x}\text{O}_{3y}$ during the growth process.....122

Figure 5.32. XRD patterns of ZnO/ZnInO heterostructure nanowires and un-doped ZnO nanowires. Both patterns match that of bulk ZnO with hexagonal structure and no peaks from Zn, In or other impurities are detected123

Figure 5.33. PL spectra of ZnO/ZnInO heterostructure nanowires and un-doped ZnO nanowires. The spectrum of the heterostructure nanowires indicates a blue-shift in the UV peak by 8 nm for the heterostructure nanowires in comparison to un-doped ZnO nanowires. This shift is attributed to the Burstein-Moss effect.....124

Figure 6.1. (a₁, b₁) FESEM images of the S- and Sn-doped ZnO nanobelts, respectively. (a₂, b₂) High-magnification FESEM image of a single S- and Sn-doped ZnO nanobelt, respectively. (a₃, b₃) EDX spectra of a single S- and Sn-doped ZnO nanobelt128

Figure 6.2. FESEM image and EDX spectrum of the un-doped ZnO nanobelts130

Figure 6.3. XRD patterns of the S-deped, Sn-doped, and un-doped ZnO nanobelts. All patterns agree with the standard card of bulk ZnO with a hexagonal structure, and no peaks from other impurities are detected. The inset shows the shifts of (101) peaks of the S- and Sn-doped ZnO nanobelts in comparison to the (101) peak of the un-doped ZnO nanobelts.....131

Figure 6.4. (a) PL spectra of the S-doped, Sn-doped, and un-doped ZnO nanobelts. The inset shows that the UV peak of Sn-doped ZnO nanobelts is blue-shifted in comparison to the un-doped ZnO nanobelts. (b) PL spectra of the S-doped ZnO nanobelts, as-grown and annealed at 600 °C for 1h. The inset shows the appearance of a UV peak at 383 nm after annealing. (c) PL spectra of the Sn-doped ZnO nanobelts, as-grown and annealed at 600 °C for 1h. The inset exhibits a blue-shift for the UV peak after annealing133

Figure 6.5. FESEM image and EDX spectrum of the S-doped ZnO nanobelts after annealing at 600 °C.....136

Figure 6.6. XRD patterns of the as-grown and annealed samples at 400 and 600 °C for 1 h in an air atmosphere. All peaks intensities increased with higher annealing temperature137

Figure 6.7. PL spectra of the S-doped ZnO nanobelts: as-grown and annealed at 400 and 600 °C for 1h in an air atmosphere. Intensity of the visible emission peaks increases with the increase of the annealing temperature. Also, the green emission peaks show a red-shift after annealing. The inset shows the appearance of a UV peak at 383 nm after annealing138

Figure 6.8. (a) Raman spectra of S-doped and un-doped ZnO nanobelts. All Raman modes of the S-doped ZnO nanobelts show a red-shift relative to the Raman modes of the un-doped ZnO nanobelts. (b) Raman spectra of the S-doped ZnO nanobelts: the nanobelts were as-grown and annealed at 400 and 600 °C for 1h in an air atmosphere. The intensity of the E₂(high) and E₁(LO) peaks increased with a higher annealing temperature. The E₂(high) peak shows a blue-shift after annealing.....139

List of Tables

Table. 2.1. Selective material parameters of ZnO 15

Table 5.1. Average Mg content in the $Zn_{1-x}Mg_xO$ nanowires grown on the various substrates and the Mg content at different locations of a single nanowires 94