II-VI Semiconductor Nanowire Array Sensors Based on Piezotronic, Piezo-Phototronic and Piezo-Photo-Magnetotronic Effects

Shuke Yan
*University of New Orleans, syan@uno.edu*

Follow this and additional works at: https://scholarworks.uno.edu/td

Part of the [Materials Chemistry Commons](https://scholarworks.uno.edu/collections/mat), and the [Semiconductor and Optical Materials Commons](https://scholarworks.uno.edu/collections/opt)

**Recommended Citation**


This Dissertation is protected by copyright and/or related rights. It has been brought to you by ScholarWorks@UNO with permission from the rights-holder(s). You are free to use this Dissertation in any way that is permitted by the copyright and related rights legislation that applies to your use. For other uses you need to obtain permission from the rights-holder(s) directly, unless additional rights are indicated by a Creative Commons license in the record and/or on the work itself.

This Dissertation has been accepted for inclusion in University of New Orleans Theses and Dissertations by an authorized administrator of ScholarWorks@UNO. For more information, please contact scholarworks@uno.edu.
II-VI Semiconductor Nanowire Array Sensors Based on Piezotronic, Piezo-Phototronic and Piezo-Photo-Magnetotronic Effects

A Dissertation

Submitted to the Graduate Faculty of the
University of New Orleans
In partial fulfillment of the
Requirements for the degree of

Doctor of Philosophy
In
Chemistry

By
Shuke Yan
B.S. Shijiazhuang Railway University, China, 2005
M.S. University of Science and Technology Beijing, China, 2008
M.S. University of New Orleans, USA, 2016

May, 2018
Acknowledgements

The research in this dissertation was conducted in the Advanced Materials Research Institute (AMRI) and the Department of Chemistry of University of New Orleans (UNO). Without the enormous help from the colleagues of AMRI, Chemistry Department, and other institutes in UNO, this research is impossible.

I would like to first and foremost express my gratitude and appreciation to my wife and my parents. Their love and unconditional support along this journey help me to complete this long study.

I gratefully thank my advisor, Prof. Weilie Zhou, for his expertise in this field, for giving the opportunity to me to pursue my Ph.D, and his continuous support during this period. He is a great advisor and always gives me invaluable suggestion in my research as well as in my life.

I would like to express sincere appreciation for my academic committee members: Prof. Mark L. Trudell, Prof. John B. Wiley, and Prof. Victor Poltavets, for their efforts in reviewing and providing very helpful suggestions on this dissertation.

Furthermore, I would like to thank Drs. Jiajun Chen, Sarah Wozny, Haiqiao Su, Satish Chandra Rai, and Zhi Zheng for their help in my research.

I would like to thank AMRI and the Department of Chemistry for their continuous support and help during my Ph.D program. I would also like to express my sincere thanks to Poncho De Leon and Jennifer Tickle for their support and help.
# Table of Contents

Table of Figures.......................................................................................................................... vi

Abstract....................................................................................................................................... xi

Chapter 1 Introduction..................................................................................................................... 1

1.1 Piezoelectricity......................................................................................................................... 1

1.2 Piezotronic Effect...................................................................................................................... 3

1.2.1 Piezotronic Effect on Metal-Semiconductor Contact ...................................................... 4

1.2.2 Piezotronic Effect on P-N Junction.................................................................................... 8

1.2.3 Applications of Piezotronic Effect...................................................................................... 10

1.3 Piezo-Phototronic Effect......................................................................................................... 15

1.3.1 Piezo-Phototronic Effect in Optoelectronic Applications................................................. 15

1.4 Overview of This Dissertation................................................................................................ 17

Reference ...................................................................................................................................... 19

Chapter 2 Synthesis and Characterization of II-VI Piezoelectric Semiconductor Nanowire Arrays......................................................................................................................... 24

2.1 Introduction............................................................................................................................ 24

2.2 Zinc Oxide Nanowire Array .................................................................................................. 24

2.2.1 Synthesis of ZnO Nanowire Array via Hydrothermal Method...................................... 26

2.2.2 Synthesis of ZnO Nanowire Array via Chemical Vapor Deposition Method .......... 29

2.2.3 Characterization of ZnO Nanowire Array ...................................................................... 37

2.3 Cadmium Selenide Nanowire Array ..................................................................................... 39

2.3.1 Synthesis of CdSe Nanowire Array ................................................................................. 41

2.3.2 Characterization of CdSe Nanowire Array .................................................................... 42

2.4 Conclusion ............................................................................................................................ 44

Reference .................................................................................................................................... 45
Chapter 3 Self-Powered Active Gas Sensors Based on Piezotronic Effect .................. 48
  3.1 Introduction ........................................................................................................ 48
  3.2 Self-Powered Gas Sensors Based on ZnO/Metal Oxide Core/Shell Nanowire Arrays .... 49
    3.2.1 Synthesis and Characterization of ZnO/Metal Oxide Nanowire Arrays ............. 50
    3.2.2 Gas Sensor Fabrication and Measurement Process ........................................ 52
    3.2.3 Results and Discussion .................................................................................... 56
    3.2.4 Conclusion ....................................................................................................... 61
  3.3 Self-Powered CdSe Nanowire Array Sensor ........................................................ 61
    3.3.1 Gas Sensor Fabrication and Measurement Process .......................................... 62
    3.3.2 Results and Discussion .................................................................................... 64
    3.3.3 Conclusion ....................................................................................................... 66
  3.4 Summary .................................................................................................................. 67
Reference ...................................................................................................................... 68

Chapter 4 Piezo-Phototronic Effect Enhanced UV/Visible Photodetector ..................... 71
  4.1 Introduction ............................................................................................................ 71
  4.2 Synthesis of ZnO/ZnSe Core/Shell Nanowire Array .............................................. 73
  4.3 Device Fabrication and Measurement Process ..................................................... 73
  4.4 Results and Discussion ......................................................................................... 74
    4.4.1 Structural Characterization ............................................................................. 74
    4.4.2 Photodetector Measurement under Different Wavelength Excitation Sources .... 76
    4.4.3 Photodetector Measurement under Piezo-Phototronic Effect ......................... 77
    4.4.4 Self-Powering Performance of Photodetector .................................................. 81
  4.5 Conclusion ............................................................................................................. 84
Reference ...................................................................................................................... 85
Chapter 5 Piezo-Magnetotronic and Piezo-Photo-Magnetotronic Effects in ZnO and ZnO/Co$_3$O$_4$ Nanowire Arrays ................................................................. 89

5.1 Introduction .............................................................................................................. 89
5.2 Experiment .................................................................................................................. 91
  5.2.1 Synthesis of ZnO Nanowire Array ................................................................. 91
  5.2.2 Synthesis of ZnO/Co$_3$O$_4$ Core/Shell Nanowire Array ............................... 91
  5.2.3 Material Characterizations .............................................................................. 92
  5.2.4 Device Fabrication and Measurement Process ............................................... 94
5.3 Results and Discussion ......................................................................................... 95
  5.3.1 Piezo-Magnetotronic Effect ............................................................................ 95
  5.3.2 Piezo-Photo-Magnetotronic Effect .................................................................. 99
5.4 Conclusion ............................................................................................................... 102
Reference ..................................................................................................................... 104

Chapter 6 Concluding Remarks .................................................................................. 107

Appendix: Copyright Permissions ............................................................................. 109

VITA ............................................................................................................................... 116
Table of Figures

Figure 1.1 Piezopotential in a wurtzite-structured ZnO nanowire. (a) Atomic model of the ZnO with wurtzite crystal. (b) The calculated distribution of the piezopotential along a ZnO NW under axial strain (left) and transverse strain (right). The color gradient represents the distribution of piezopotential in which red indicates positive piezopotential and blue indicates negative piezopotential (Adapted with permission from reference 15). ................................................................. 3

Figure 1.2 Schematic of energy diagram of the metal-semiconductor contact under the piezopotential. (a) The negative piezopotential is induced at the interface and increases the local SBH. (b) The positive piezoelectric polarization ionic charges are accumulated at the interface and decrease the local SBH. The color gradients present the distribution of the piezopotential, in which red indicates positive piezopotential and blue indicates negative piezopotential (Adapted with permission from reference 15). .................................................................................. 4

Figure 1.3(a) Space charge distribution; (b) electric field, and (c) energy-band diagram for ideal metal-semiconductor Schottky contacts with the presence of piezoelectric polarization charges at the applied voltage V=0 (thermal equilibrium). The dashed lines indicate the electric field and energy band with the absence of piezoelectric charges (Adapted with permission from reference 15). ........................................................................................................... 7

Figure 1.4 (a) The band diagrams of the p-n junction with and without the effect of positive piezopotential. (b) The band diagrams of the p-n junction with and without the effect of negative piezopotential. The color gradients present the distribution of the piezopotential, in which red indicates positive piezopotential and blue indicates negative piezopotential. The band diagrams for the p–n junction with and without the presence of the piezotronic effect are shown using the red solid and black dashed curves, respectively. Ef, n and Ef, p are the Fermi levels in n and p type materials, respectively. E0 and Ei are the vacuum level and intrinsic Fermi level, respectively. The black dots and empty circles represent the free-charge carriers in the semiconductor. Symbols ‘+’ and ‘−’ represent the ionized donors and acceptors in respective regions (Adapted with permission from reference 15). ................................................................. 9

Figure 1.5 Changes of transport characteristics of an Ag/ZnO NW/Ag device from symmetric I-V characteristic (black) to asymmetric rectifying behavior when stretching (red) and compressing (green) the NW (Adapted with permission from reference 17). .............................................. 11
Figure 1.6 Comparison between a traditional field effect transistor and a strain-gated transistor (Adapted with permission from reference 15). .......................................................... 13

Figure 2.1 Atomic structure model of wurtzite ZnO nanowire. ................................................. 25

Figure 2.2 Attachment of hexamine to the non-polar facets of the zincite crystal allows the growth of the crystal in the (0001) direction. (a) hexagonal ZnO crystal (b) possible attachment of hexamine on to the non-polar facets leaving the polar face exposed allowing further crystal growth along the c-direction. (Reproduced with permission from reference 11). ................. 27

Figure 2.3 (a) Top-view and (b) cross-section view FESEM images of vertically aligned ZnO nanowire arrays. .................................................................................................................. 28

Figure 2.4 Schematic illustration of the growth of dimension-controlled NWs. (a) The size of catalysts for NW diameter control. (b) The growth time for NW length control. .................... 31

Figure 2.5 Schematic of the set-up used for the growth of ZnO NW arrays by CVD method. ................................. 33

Figure 2.6 The heating temperature profiles of the two-zone furnace ............................................. 34

Figure 2.7 (a) FESEM images of the as-grown ZnO NW arrays via VLS. (b) The multi-prong root growth process of ZnO NW arrays. .................................................................................... 35

Figure 2.8(a) FESEM images of the as-grown ZnO NW array via VS. (b) Schematic diagram of the VS growth process of ZnO NW arrays. R_{Zn} and R_{O} represent the absorption rates of Zn atoms and O atoms in the Zn/ZnO_x droplet, respectively ........................................ 36

Figure 2.9 (a) TEM image of a single ZnO NW with corresponding (b) SAED pattern and (c) EDS spectrum. (d) XRD pattern of pristine ZnO NW arrays. ......................................................... 38

Figure 2.10 (a) Schematic crystal structure of CdSe NW along <0001> direction; (b) strain and corresponding piezopotential distribution on the surface of NW under a bending force 80 nN in COMSOL simulation; (c) piezopotential distribution under normal force ranging from 100 to 400 nN. Geometry of the NW used in the simulation is diameter D = 60 nm and length L = 250 nm (Adapted with permission from reference 1) ..................................................................................... 39

Figure 2.11 Schematic of the synthesis procedure of CdSe NW arrays. ............................................. 42

Figure 2.12 (a) Top-view and (b) tilt-view FESEM images of CdSe NW arrays. (c) Low magnification TEM image of a single CdSe NW with corresponding (d) SAED pattern .......... 43
Figure 2.13(a) XRD patterns of mica substrate and CdSe NW array on mica. (b) EDS spectrum of a single CdSe NW .......................................................... 44

Figure 3.1 FESEM images with corresponding EDS spectra of (a) ZnO/SnO$_2$, (b) ZnO/In$_2$O$_3$ and (c) ZnO/WO$_3$ core/shell NW arrays ........................................................................... 52

Figure 3.2 Schematic of gas sensor fabrication based on core/shell NW arrays .................. 53

Figure 3.3 Photo image of the homemade gas sensor testing platform .............................. 54

Figure 3.4 The sensitivities of gas sensors based on ZnO/SnO$_2$, ZnO/In$_2$O$_3$ and ZnO/WO$_3$ core/shell NW arrays responding to (a) NO$_2$ and (b) H$_2$S gases .......................................................... 56

Figure 3.5 Piezoelectric output voltages of ZnO/SnO$_2$ NW array gas sensor in (a) dry air, (b) 1000 ppm NO$_2$ and (c) 1000 ppm H$_2$S under repeatedly compressive stress at room temperature .................................................................................. 57

Figure 3.6 The working mechanism of the self-powered ZnO/SnO$_2$ NW arrays gas sensor. ...... 58

Figure 3.7 Piezoelectric output voltages of ZnO/In$_2$O$_3$ gas sensor in (a) dry air, (b) 1000 ppm NO$_2$ and (c) 1000 ppm H$_2$S under repeatedly compressive stress at room temperature ........... 60

Figure 3.8 Piezoelectric output voltages of ZnO/WO$_3$ gas sensor in (a) dry air, (b) 1000 ppm NO$_2$ and (c) 1000 ppm H$_2$S under repeatedly compressive stress at room temperature ............. 61

Figure 3.9 Schematic of gas sensor fabrication based on CdSe NW array ......................... 62

Figure 3.10 The sensitivity of CdSe NW array gas sensor responding to (a) NO$_2$ and (b) NH$_3$ gases ................................................................................................................. 64

Figure 3.11 Piezoelectric output voltages of CdSe gas sensor in (a) dry air, (b) 1000 ppm NO$_2$ and (c) 1000 ppm NH$_3$ under repeatedly compressive stress at room temperature .................. 65

Figure 4.1 Schematic of photodetector fabrication and the measurement process. (a) ZnO nanowire array is grown on ZnO-coated ITO glass via chemical vapor deposition method. (b) ZnSe is coated on ZnO nanowires through pulsed laser ablation. (c) The as-synthesized ZnO/ZnSe nanowire array is integrated using Ag-coated polyester as top electrode. (d) The device and measurement setup. The cross section schematic of the device is shown in the inset. ............................................................................................................. 74
Figure 4.2 Top view FESEM images of (a) ZnO nanowire array, and (b) ZnO/ZnSe core/shell nanowire array, (c) TEM image of a single ZnO/ZnSe nanowire, and (d) EDS result on the single ZnO/ZnSe nanowire. 

Figure 4.3 (a) The on-off response of the device under red excitation source at 1V bias. (b) Typical I-V measurement of the photodetector under different excitation sources without load. 

Figure 4.4 Typical I-V measurement of the photodetector under varying compressive loads and illumination of (a) red light, (b) green light, (c) blue light and (d) UV light, respectively. 

Figure 4.5 (a) The compressive load dependences of photocurrent response, (b) the sensitivity, (c) the responsivity and (d) the percentage change in responsivity of the detector with respect to compressive loads under different wavelength excitation sources from UV to red. 

Figure 4.6 The photocurrent response of the device under varying compressive loads at no external bias under (a) red, (b) green, (c) blue and (d) UV excitation source. 

Figure 4.7(a) Energy band diagram of a strain-free type-II ZnO/ZnSe heterojunction before the Ag-coated electrode contact is made. The solid lines (green and blue) show the bands of ZnSe and ZnO, and the black dashed line shows Fermi level for both ZnO and ZnSe. (b) Energy band diagram of a strain-free ZnO/ZnSe based photodetector. Ag-coated electrode attached to the top of the ZnSe shell promotes Fermi level realignment that induces band bending. Energy band diagrams of the photodetector (c) under light illumination only and (d) under light illumination and compressive loads, which leads to a piezopotential-induced band bending. 

Figure 4.8 Simulated piezo-potential distribution in ZnO core of a single ZnO/ZnSe core/shell nanowire under (a) shear mode (uniaxial compression combined with bending), (b) uniaxial compression mode, and (c) bending mode. The vertical color gradient represents the distribution of piezo-potential in the interior of ZnO nanowire. This simulation neglects any piezo-potential contribution from the zinc-blend ZnSe shell. 

Figure 5.1 FESEM images of (a) pristine ZnO NWs and (b) ZnO/Co$_3$O$_4$ core/shell NWs, insets in a and b are the high-resolution images. (c) TEM image of a single ZnO/Co$_3$O$_4$ core/shell NW with corresponding (d) SAED pattern and (e) EDS spectrum. (f) XRD pattern of pristine ZnO NWs and ZnO/Co$_3$O$_4$ core/shell NWs. 
Figure 5.2 Schematic illustration of the device fabrication and the measurement process. (a) as-synthesized ZnO or ZnO/Co$_3$O$_4$ NWs on ITO glass substrate, (b) a ~2 µm PMMA layer was spin-coated onto the NWs, (c) the device was integrated with Ag-coated top electrode and (d) the device was located on homemade stage where load was applied on top of the device, UV light was illuminated from the bottom of the device and magnetic field was applied perpendicularly to the NWs. ................................................................. 94

Figure 5.3 I-V characteristics of ZnO NWs device under (a) 0 N (b) 0.5, (c) 1 and (d) 1.5 N stress. (e) The summary of the peak current difference of the device under various stresses. (f) Schematics of energy bands alignment and electron movement under magnetic field which is directed perpendicularly out of the screen. ................................................................. 97

Figure 5.4 I-V characteristics of ZnO/Co$_3$O$_4$ NWs device under (a) 0 N (b) 0.5, (c) 1 and (d) 1.5 N stress. (e) The summary of the peak current difference of the device under various stresses. (f) Schematics of energy bands alignment and electron movement under magnetic field which is directed perpendicularly out of the screen. ................................................................. 98

Figure 5.5 I-V characteristics of ZnO NWs device under UV illumination and (a) 0 N (b) 0.5, (c) 1 and (d) 1.5 N stress. (e) The summary of the peak current difference of the device under various stresses. (f) Schematics of energy bands alignment and electron movement under magnetic field which is directed perpendicularly out of the screen. ................................................................. 99

Figure 5.6 I-V characteristics of ZnO/Co$_3$O$_4$ NWs device under UV illumination and (a) 0 N (b) 0.5, (c) 1 and (d) 1.5 N stress. (e) The summary of the peak current difference of the device under various stresses. (f) Schematics of energy bands alignment and electron movement under magnetic field which is directed perpendicularly out of the screen. ................................................................. 101
Abstract

With the rapid progress of nanotechnologies, there are two developing trends for the next generation of sensors: miniaturization and multi-functionality. Device miniaturization requires less power consumption, or even self-powered system. Multi-functional devices are usually based on multi-property coupling effects. Piezoelectric semiconductors have been considered to be potential candidates for self-powered/multi-functional devices due to their piezotronic coupling effect. In this dissertation, ZnO and CdSe nanowire arrays have been synthesized as the piezoelectric semiconductor materials to develop the following self-powered/multi-functional sensors: (1) self-powered gas sensors of ZnO/SnO₂, ZnO/In₂O₃, ZnO/WO₃ and CdSe nanowire arrays have been assembled. All these gas sensors are capable of detecting oxidizing gas and reducing gas without any external power supply owing to piezotronic effect which can convert mechanical energies to electrical energy to power the sensors; (2) a self-powered ZnO/ZnSe core/shell nanowire array photodetector has been fabricated. This photodetector is able to detect the entire range of the visible spectrum as well as UV light because of its type II heterostructure. The absolute sensitivity and the percentage change in responsivity of the photodetector were significantly enhanced resulting from the piezo-phototronic effect. The photodetector also exhibited self-powered photodetection behavior; (3) three dimensional nanowire arrays, such as ZnO and ZnO/Co₃O₄, have been synthesized to investigate piezo-magnetotronic and piezo-photo-magnetotronic effects. Under magnetic field, the magnetic-induced current of ZnO nanowire array decreased as magnetic field increased, and the current difference was magnified by one order of magnitude caused by piezo-magnetotronic effect through applying a stress. In contrast, under UV light illumination, the current response increased with an increment of magnetic field. The current difference was enhanced by at least two orders of magnitude
attributed to piezo-photo-magnetotronic effect. Furthermore, ZnO/Co$_3$O$_4$ core/shell structure was employed to further improve the magnetic-induced current difference. This phenomenon projects a potential for multi-functional piezo-magnetotronic and piezo-photo-magnetotronic device development.

**Keywords:** Piezotronic, Piezo-phototronic, Piezo-magnetotronic, Piezo-photo-magnetotronic, self-powered, nanowire array, gas sensor, photodetector.
Chapter 1 Introduction

1.1 Piezoelectricity

The word *piezoelectricity* is derived from the Greek, meaning electricity resulting from pressure and heat. It is used to describe a reversible ability of certain dielectric materials in which the electric charge accumulates on their surfaces as a result of applying a mechanical stress, or vice versa.\(^1\) Piezoelectricity is a linear electromechanical interaction between the induced charges and the applied mechanical stress. It was first discovered by French physicists Jacques and Pierre Curie in 1880.\(^2\) After that, it has been further studied in laboratories for the next few decades. Its first practical application as a piezoelectric device\(^3\) was developed during World War I, which attracted intense attention and accelerated its development. Over the past few decades, innovative piezoelectric materials have been explored\(^4-7\) and widely employed in ultrasonic transducers,\(^8\) electromechanical sensors,\(^9\) actuators\(^10\) and piezoelectric resonators\(^11\). However, these piezoelectric materials are electrical insulating materials and are relatively useless for electronics because the modern electronics of silicon-based complementary metal–oxide–semiconductor (CMOS) technology requires direct control of the operation of CMOS by electrical driven charge and/or mechanical action. Instead, piezoelectric semiconducting materials with an asymmetric wurtzite structure are the optimal choice for the modern electronics since they can generate an electric signal according to mechanical action.

The first groundbreaking research of piezoelectricity in semiconductor was the invention of piezoelectric nanogenerator based on ZnO nanowire (NW) array by Prof. Zhong Lin Wang in 2006,\(^12\) which explored a novel approach for generating electric energy resulting from mechanical energy on nano-scale level. ZnO, as a well-known II-VI group metal oxide semiconductor, has both semiconducting and piezoelectric properties resulting from its
asymmetric wurtzite crystal structure.\textsuperscript{13} Wurtzite crystal structure has a hexagonal architecture with a huge anisotropic property in directions of perpendicular and parallel to the c-axis direction where the Zn\textsuperscript{2+} cations and O\textsuperscript{2-} anions are tetrahedrally coordinated and the cation center overlaps with the anion center.\textsuperscript{14} When a mechanic stress is applied on the tetrahedron, the centers of the positive ions and negative ions are relatively displaced which generates a dipole moment as shown in Figure 1.1a.\textsuperscript{15} The sum total of all the dipole moments by all the molecular units along the nanowire gives rise to a macroscopic potential difference along the straining direction which is called piezoelectric potential (piezopotential). Piezopotential, induced by the mechanical deformation, is capable of forcing the free electrons to flow in the external circuit which is the fundamental of the piezoelectronics.\textsuperscript{16} Figure 1.1b displays the distribution of piezopotential along a c-axis ZnO NW under axial strain and transverse strain calculated by numerical methods. Under axial strain, the piezopotential of the NW continuously increases/decreases from one end to the other because the electrons flow from one end to the other and the electron energy reversely continuously decreases/increases. In a transversely deformed NW, the piezopotential increases/decreases from one side to the other when the electrons flow from one side to the other and the electron energy reversely continuously decreases/increases from one side to the other.
1.2 Piezotronic Effect

Piezotronic effect is a two-way coupling effect between piezoelectricity and semiconductor properties in semiconductor materials with asymmetric crystal structure. It is using the strain-induced piezopotential in semiconductors as a "gate" voltage to tune/control the charge carrier transport properties. The strain-induced piezopotential generation and redistribution of free charge carries is able to modify the local Schottky-barrier height (SBH) between the piezoelectric semiconductor and the metal electrodes or the energy bands near the...
interface of p-n junction, and then to further control charge carrier transport across metal-semiconductor (M-S) barrier or p-n junction. This effect in M-S contact and p-n junction and its applications will be described in details to quantitatively understand the piezotronic effect.

### 1.2.1 Piezotronic Effect on Metal-Semiconductor Contact

![Diagram of energy diagram of the metal-semiconductor contact under the piezopotential](image)

**Figure 1.2** Schematic of energy diagram of the metal-semiconductor contact under the piezopotential. (a) The negative piezopotential is induced at the interface and increases the local SBH. (b) The positive piezoelectric polarization ionic charges are accumulated at the interface and decrease the local SBH. The color gradients present the distribution of the piezopotential, in which red indicates positive piezopotential and blue indicates negative piezopotential (Adapted with permission from reference 15).

The metal-semiconductor (M-S) contact is one of the fundamental contacts in electronics and optoelectronics, which can significantly redistribute the charge carriers between an M-S interface because the bands of the metal overlaps with that of the semiconductor. When a metal contacts a semiconductor, an M-S interface will be formed. Fermi levels on both the metal and the semiconductor must be aligned to reach a new thermal equilibrium, resulting in a net charge carrier flow at the M-S interface. Electrons will transfer from the semiconductor (for the n-type semiconductor) into the metal if the work function of the metal is appreciably larger than the electron affinity of the semiconductor and thus a depletion region will be created in the
semiconductor close to the M-S interface. This depletion area can change the energy bands of the semiconductor near the interface and then generate a Schottky barrier. Ideally, the SBH equals the difference of the work function of the metal and the electron affinity of the semiconductor and determinates the charge carrier transport at the M-S interface. If the external positive bias is applied on the metal, the current can only pass through the barrier as the bias is larger than a certain threshold value of $\phi_i$.

If the external stress is applied on the piezoelectric semiconductor, piezopotential will be generated inside the semiconductor. If the negative piezopotential is induced near the M-S interface, it will force the electrons to flow away from the interface, and thus expand the depletion region and increase the local SBH of the M-S (Figure 1.2a). If the positive piezopotential is induced at the M-S interface, the electrons will be attracted to the interface and thus narrow the depletion region and decrease the local SBH of the M-S contact (Figure 1.2b). SBH of the M-S contact is directly relative to the transport of charge carriers flowing across the Schottky barrier. Therefore, the strain-induced piezopotential is capable of significantly and effectively modifying the characteristics of the M-S contact based on the crystallographic orientation of the piezoelectric material and the polarity of the applied stress. In other words, it can modulate the local contact characteristics, and consequently, to modify the transport of the charge carries by controlling the magnitude and direction of the external stress.

Figure 1.3 displays the space charge distribution, electric field and energy band diagram in the M-S contact with the presence of piezoelectric charges without bias applied by ignoring surface states and other anomalies, where $W_n$ is the width of the region where ionized donors are distributed in n type ZnO. When the external stress is applied on ZnO, the induced piezopotential will change not only the local SBH mentioned above, but also the width of the depletion region.
The charge carrier flowing across the M-S contact is dominated by the majority carriers (i.e., electrons here) according to the diffusion theory for the Schottky barrier. The saturation current density \( J_D \) with the absence of the piezoelectric polarization charge can be calculated as below:

\[
J_D \approx q^2 D_n N_C (kT)^{-1} \times \sqrt{2qN_D (\Psi_{bi0} - V) \times \varepsilon_s^{-1}} \times e^{-q\Phi_{Bn0}/(kT)} \quad (1.1)
\]

Where \( \varepsilon_s \) is the permittivity of the semiconductor, \( D_n \) is the diffusion coefficient for electrons, \( N_C \) is the effective density of states in the conduction band, and \( N_D \) is the donor concentration in the semiconductor. \( \Psi_{bi0} \) and \( \Phi_{Bn0} \) are the built-in potential and SBH with the absence of piezoelectric polarization charges, respectively. The saturation current density \( J_D \) and the current \( J_n \) under the forward bias can be expressed as

\[
J_D \approx q^2 D_n N_C (kT)^{-1} \times \sqrt{2qN_D (\Psi_{bi} - V) \times \varepsilon_s^{-1}} \times e^{-q\Phi_{Bn}/(kT)} \quad (1.2)
\]

\[
J_n \approx J_D \times \left( e^{qV/(kT)} - 1 \right) \quad (1.3)
\]

The effect of the piezopotential can be considered as perturbation to the conduction band edge. The piezopotential-induced change of the effective SBH is derived as \( \Phi_{Bn} = \Phi_{Bn0} - q^2 \rho_{piezo} - W_{piezo}^2 (2\varepsilon_s)^{-1} \), where piezoelectric polarization charges are distributed in the region with a width of \( W_{piezo} \) near the barrier interface. According to the conventional piezoelectric theory, the piezoelectric polarization charges occupied region is much smaller than the volume of the bulk crystal. Therefore, it is reasonable to assume that the piezoelectric polarization charges are distributed at only the surface region with the zero thickness of the bulk piezoelectric semiconductor, although it is not true for NW devices. The current density flowing across the M-S contact can be expressed as

\[
J_n \approx J_{D0} \times e^{q^2 \rho_{piezo} W_{piezo}^2 (2kT \varepsilon_s)^{-1}} \times e^{(qV)/(kT)} \quad (1.4)
\]

For metal-ZnO NW contact, if the induced strain is \( s_{33} \) along the c-axis of the ZnO NW, a more specific expression can be rewritten to reflect the effect of piezoelectric polarization
charges on M-S contact, the piezoelectric polarization can be expressed as $P_z = e_{33}s_{33} = q\rho_{\text{piezo}}W_{\text{piezo}}$, where $\rho_{\text{piezo}}$ represents the density of created piezoelectric polarization charges (in units of electron charge). The current density across the M-S contact based on ZnO NW can be rewritten as

$$J \approx J_{D0} \times e^{q^2e_{33}s_{33}W_{\text{piezo}}(2kT\varepsilon)^{-1}} \times e^{qV/kT-1} \quad (1.5)$$

Figure 1.3(a) Space charge distribution; (b) electric field, and (c) energy-band diagram for ideal metal-semiconductor Schottky contacts with the presence of piezoelectric polarization charges at the applied voltage $V=0$ (thermal equilibrium). The dashed lines indicate the electric field and energy band with the absence of piezoelectric charges (Adapted with permission from reference 15).
It can be concluded that the current flowing across the M-S contact is clearly related to the magnitude and the polarity of the induced strain. The current decreases when the negative piezoelectric polarization charges (negative $\rho_{\text{piezo}}$) are generated near the local Schottky barrier due to compressive strain (negatives $\varepsilon_{33}$). A similar conclusion can be drawn when the polarity of the induced strain is positive due to tensile strain.$^{18}$

## 1.2.2 Piezotronic Effect on P-N Junction

The p-n junction is also a common and important fundamental contact in electronics and optoelectronics. If a p type semiconductor contacts an n type semiconductor, the free charge carriers (i.e., holes in the p type semiconductor and electrons in the n type semiconductor) tend to diffuse across the p-n junction to re-balance the local potential to reach a thermal equilibrium. This process leaves ionized donors and acceptors behind and results in a charge depletion area. The ionized donors and acceptors in the depletion region will generate an electric field which forces the free charge carriers to drift reversely until the drift current balances the diffusion current to reach a new thermal equilibrium. The depletion region is able to largely improve the piezoelectric effect since this carrier-free region tends to significantly preserve the piezoelectric polarization charges, instead of being screened by local residual free carriers. To explain it, the p-n junction is ideally treated as a homojunction where the bandgaps of p and n type materials are the same, and only the n type material is piezoelectric. When the n type semiconductor is deformed by the external stress, and if the induced piezopotential near the junction in n type semiconductor is positive as shown in Figure 1.4a, the positive piezopotential will attract the electrons to the end of the n type semiconductor near the contact and the electrons will be trapped or accumulated in the interface, resulting in a dip in the local bands. This dip in the local profile might be used to modulate the electron-hole recombination rate as well as the mobility.
and transportation of the charged carriers in the interface, and finally enhance the device performance. If the induced piezopotential near the junction in n type semiconductor is negative as shown in Figure 1.4b, the negative piezopotential will force the electrons away from the interface and increase the depletion region of electrons, which will generate a shoulder in the local bands. This shoulder in the local bands will suppress the recombination of the electrons and the holes. Similar conclusion can be made to cases of p type piezoelectric semiconductor in p-n homojunction.

![Figure 1.4](image.png)

**Figure 1.4** (a) The band diagrams of the p-n junction with and without the effect of positive piezopotential. (b) The band diagrams of the p-n junction with and without the effect of negative piezopotential. The color gradients present the distribution of the piezopotential, in which red indicates positive piezopotential and blue indicates negative piezopotential. The band diagrams for the p–n junction with and without the presence of the piezotronic effect are shown using the red solid and black dashed curves, respectively. \(E_f\), \(n\) and \(E_f\), \(p\) are the Fermi levels in \(n\) and \(p\) type materials, respectively. \(E_0\) and \(E_i\) are the vacuum level and intrinsic Fermi level, respectively. The black dots and empty circles represent the free-charge carriers in the semiconductor. Symbols '+' and '-' represent the ionized donors and acceptors in respective regions (Adapted with permission from reference 15).

In order to reveal the piezotronic effect in p-n junctions, it is assumed based on Shockley theory that the p type semiconductor is non-piezoelectric and n type ZnO NW semiconductor is piezoelectric. If the ZnO NW is compressed along the c-axis, the positive charges are generated at the ZnO side near the p-n junction. According to the abrupt junction model, the impurity
concentration in a p-n junction changes abruptly from the acceptor $N_A$ to the donor $N_D$. The built-in potential is expressed by the following equation:

$$
\Psi_{bi} = q(2\varepsilon_s)^{-1} \left( N_A W_{Dp}^2 + \rho_{\text{piezo}} W_{\text{piezo}}^2 + N_D W_{Dn}^2 \right)
$$

(1.6)

Where $N_D(x)$ is the donor concentration, $N_A(x)$ is the acceptor concentration, and $W_{Dp}$ and $W_{Dn}$ are the depletion layer widths in the p-side and the n-side, respectively.

The above equation 1.6 indicates that the built-in potential can be tuned by the strain-induced piezopotential, and the total current density of the device based on this p-n junction is expressed by the following equation:

$$
J = J_{C0} \times e^{q^2 \rho_{\text{piezo}} W_{\text{piezo}}^2 (2kT\varepsilon_s)^{-1} e^{qV(kT)^{-1}} - 1}
$$

(1.7)

Where $J_{C0}$ is the saturation current density without the piezopotential. This illustrates that the current flowing across the p-n junction is an exponential function of the density of local piezoelectric charges and the sign of which depends on the type of strain. The transportation of the charge carriers across the p-n junction can be significantly tuned by the magnitude and the sign of the strain (compressive or tensile).\textsuperscript{18}

1.2.3 Applications of Piezotronic Effect

When external mechanical energy is applied on piezoelectric semiconductor, a piezopotential can be created inside because of the polarization of the non-mobile acceptors and donors. Considering the fact that the magnitude and the polarity of the strain-induced piezopotential can be controlled by external mechanical stress, the piezopotential can be applied as a control signal to effectively modulate the transport characteristics of charge carriers by controlling the magnitude and the polarity of the induced strain, which is the fundamental
principle for strain-gated piezotronic devices such as piezotronic diodes,\textsuperscript{19–23} piezotronic transistors,\textsuperscript{24–26} active sensors,\textsuperscript{27–31} and energy harvesting devices.\textsuperscript{30–34}

![Image of Figure 1.5](image)

**Figure 1.5** Changes of transport characteristics of an Ag/ZnO NW/Ag device from symmetric $I$-$V$ characteristic (black) to asymmetric rectifying behavior when stretching (red) and compressing (green) the NW (Adapted with permission from reference 17).

### 1.2.3.1 Piezotronic Diodes

A simple piezotronic device is a polarity switchable diode. Figure 1.5 displays a ZnO NW diode which is contacted with two Ag electrodes to form two ZnO-Ag Schottky barriers. The original symmetric $I$-$V$ curve of the diode illustrates that the SBHs of the two ZnO-Ag
contacts are almost same, and it is an equivalent back-to-back Schottky diode. When the ZnO NW was stretched, a negative piezopotential (presented by blue color in the inset of Figure 1.5) was generated at the interface of right-hand ZnO-Ag contact which raised the SBH (presented by a large diode symbol in the inset of Figure 1.5) and a positive piezopotential was generated at the interface of left-hand ZnO-Ag contact, which was partially screened by free electrons resulting in an almost unchanged SBH (presented by a small diode symbol in the inset of Figure 1.5). The current transport was mainly determined by the reverse biased SB. When it was under the positive bias voltage and the right-hand SB was the reverse biased SB, the current of the diode significantly decreased. When it was under the negative bias voltage and the left-hand SB was under reverse biased voltage, the current of the diode was almost same with that of the diode without straining. When the ZnO NW was compressed, the inverse piezopotential was generated, resulting in a huge decrement of the current in the negative bias voltage and the almost unchanged current in the positive bias voltage.
1.2.3.2 Piezotronic Transistors

Traditional field effect transistors (FET) shown in Figure 1.6 usually have three terminals: a source, a drain, and a gate. The gate voltage is applied either from the top of a gate electrode or from the bottom substrate to control the flow of electrons/holes from the source to the drain by affecting the size and shape of the conductive channel between the source and the drain of the FET. Alternatively, piezotronic transistor based on a signal ZnO NW, as shown in Figure 1.6, has only two terminals: a source and a drain, the gate voltage can be replaced by the strain-induced piezopotential along ZnO NWs. The induced inner-crystal piezopotential can act as a gate voltage to control/tune the charge transport which flows across a metal-semiconductor (M-S) interface or a p-n junction. This advantage makes it possible to fabricate a high-density NWs matrix device in electro-mechanical transduction.
1.2.3.3 Piezotronic Sensors

Sensors are widely used in our daily life and they are usually based on ohmic-contact or Schottky-contact. The sensitivity of ohmic-contact based sensors depends on the bulk channel modification by adsorption of surface charged/polar species, and the sensitivity of Schottky-contact based sensors can be tuned by modulating the SBH at the local interface through adsorption/desorption of the detected charged/polar species, so the sensitivity of Schottky-contact based sensors depends on the SBH. If the SBH is too small, it is insensitive to variation of adsorbed species, and if the SBH is too large, the current is blocked to flow through the barrier, therefore, it is important for sensors to optimize the SBH. The piezoelectric semiconductors are considered as one of the most promising materials for light, gas and biochemical sensing, because the strain-induced piezopotential inside piezoelectric semiconductors can be utilized to tune the SBH of metal-semiconductor contact effectively and then to enhance the sensitivity and improve response time.

1.2.3.4 Energy Harvesting Devices

Miniaturization is one of the major development directions of the modern electronic technology. However, a miniaturized system is composed of not only a miniaturized device but also a miniaturized battery. The miniaturized battery significantly limits the lifetime of the battery, thus the working time of the system. Therefore, it is highly desirable for the system to explore novel technologies to convert ambient energies, such as mechanical energy, vibrational energy and hydraulic energy, into electrical energy to power the system without a battery. The first energy harvesting device based on piezotronic effect is the ZnO NWs nanogenerator (NG). Once a stress is applied on piezoelectric materials, a strain-induced piezopotential is generated and it can drive the free charge carriers in the external load to flow from one end to the other to
screen the piezopotential and achieve a new equilibrium, and the transient flow of the charge carriers results in a current flow.\textsuperscript{38} Therefore, NGs are able to convert ambient mechanical energy into electricity, which offers a great potential for self-powered sensing, wireless remote system, charging batteries and powering small electronic device.\textsuperscript{39–43}

1.3 Piezo-Phototronic Effect

Piezo-phototronic effect was first coined in 2010\textsuperscript{44} which is a three way coupling among piezoelectricity, semiconductor behavior, and photon excitation characteristics of piezoelectric semiconductors. When light illuminates on a material which simultaneously has piezoelectricity, photo excitation and semiconductor properties, numerous photo-induced electron-hole pairs are generated inside the semiconductor due to its optoelectronic effect. When an external mechanical stress is applied on the semiconductors, the deform-induced piezoelectric potential is generated in the piezoelectric material near the M-S Schottky contact or p-n junction, and the localized piezoelectric polarization charges can drastically tune/control the generation, separation, recombination and transport of the photo-induced charge carriers in M-S Schottky contact or p-n junction to significantly improve the performance of optoelectronic devices, this is the fundamental principle of piezo-phototronics.

1.3.1 Piezo-Phototronic Effect in Optoelectronic Applications

Traditional optoelectronic devices are controlled by electrical signal, however, the optoelectronic devices based on piezo-phototronic effect use strain-induced piezopotential as the controlling signal which can be controlled by the external mechanic stress. After its first application as a ZnO-based UV photodetector in 2010,\textsuperscript{44} the piezo-phototronic effect has widely been studied to improve the performance of optoelectronic devices,\textsuperscript{18,45,46} such as solar cells,\textsuperscript{47,48}
light emitting diodes (LED),\textsuperscript{49,50} electrochemical processes,\textsuperscript{51} and photodetectors,\textsuperscript{52,53} through tuning and controlling charge carrier generation, separation, transport, and/or recombination.\textsuperscript{54}

1.3.1.1 Piezo-Phototronic Effect Enhanced Photodetectors

Photodetectors operate on the basis of the separation of photo-induced electron-hole pairs by Schottky barriers. For photodetectors based on Schottky barrier, the SBH determines its detecting performance, and its performance can be improved through tuning the SBH. For instance, the photoresponse of a ZnO-Au ultraviolet (UV) detector can be enhanced by applying strain-induced piezopotential, which promotes the generation, separation and transport of the photoexcited electron-hole pairs.\textsuperscript{55} The photoresponse and sensitivity of this UV detector are enhanced by 440\% and 500\%, respectively, when a stress is applied to the ZnO NW.

1.3.1.2 Piezo-Phototronic Effect Enhanced Light-emitting Diodes

The operation of a light-emitting diode (LED) is based on the carrier injection, recombination and extraction. It is reported that the piezo-phototronic effect can effectively enhance the external efficiency of a n-type ZnO NW/p-type GaN substrate LED.\textsuperscript{56} The strain-induced piezoelectric potential in the ZnO NW acts as a gate voltage to effectively modulate the injection, transport and recombination of electron-hole pairs, and the emission intensity and injection current have been enhanced by a factor of 17 and 4, respectively. The reason is that the local biased voltage increased due to the band modification caused by piezopotential and the trapping of free carries at the interface of p-n junction.

1.3.1.3 Piezo-Phototronic Effect Enhanced Solar Cells

Solar cell is one of the most commonly used optoelectronic applications. The electricity output of solar cell results from the generation, separation, transport of the photon-generated
electron-hole pairs at the M-S contact or the interface of the p-n junction. As discussed in the previous sections, the piezoelectric potential can effectively tune the photon-generated carriers separation, which can be used to enhance the solar cell performance. It has been demonstrated in an n-type CdS/p-type Cu$_2$S coaxial NW solar cell.$^{57}$ The core CdS NW is a piezoelectric semiconductor with noncentral wurtzite structure. When a stress is applying on CdS NW, the piezopotential created in the CdS NW has a strong effect on the carrier generation, separation, recombination and transport, thus improving the performance of the solar cell.

### 1.4 Overview of This Dissertation

This dissertation includes two major sections. The first section (Chapter 2) focuses on the synthesis and characterization of three dimensional II-VI piezoelectric semiconductor nanowires (ZnO and CdSe nanowires). The second section (Chapters 3, 4 and 5) focuses on the applications of CdSe, ZnO and ZnO-based core/shell nanowires as gas sensor, photodetector, and multi-functional detector. A short description of each chapter is presented as below.

**Chapter 2** will address the fabrication methods of three dimensional II-VI piezoelectric semiconductor nanowires (ZnO and CdSe nanowires). ZnO NW arrays have been grown on different substrates via different method and their characteristics have been investigated. In addition, well-aligned CdSe NW arrays have been synthesized via chemical vapor deposition (CVD) method, and the structure has been studied.

In **Chapter 3**, gas sensors based on ZnO/SnO$_2$, ZnO/In$_2$O$_3$, ZnO/WO$_3$ core/shell heterostructures and CdSe NW arrays have been integrated. All these gas sensors can be used to detect oxidizing gas and reducing gas with/without any external power supply due to piezotronic effect. Based on these results, the piezopotential created inside ZnO and CdSe NW arrays can be
used as self-powered energy source to develop other self-powered systems, such as self-powered photodetector and self-powered multi-functional device.

In **Chapter 4**, a high-performance photodetector based on ZnO/ZnSe heterostructure core/shell nanowire array will be demonstrated, and its performance and self-powered behavior will be discussed in detail. The photodetector can be used to detect the entire range of the visible spectrum, from Blue to Red excitation source, as well as UV light. Moreover, the photodetector can exhibit self-powered photodetection behavior under UV/visible light illumination.

In **Chapter 5**, the multi-field coupling effects among magnetic field, piezoelectricity and photoexcitation will be explored in ZnO and ZnO/Co$_3$O$_4$ NW arrays. The magnetic-induced current response can be magnified by one order and two orders of magnitude due to piezo-magnetotronic effect and piezo-photo-magnetotronic effect, respectively. Moreover, ZnO/Co$_3$O$_4$ core/shell heterojunction can largely improve the current response.
Reference


(41) Granstrom, J.; Feenstra, J.; Sodano, H. A.; Farinholt, K. Energy Harvesting from a


Chapter 2 Synthesis and Characterization of II-VI Piezoelectric Semiconductor Nanowire Arrays

2.1 Introduction

The past decade has witnessed dramatic advances in the development and applications of piezotronics based on II-VI wurtzite semiconductors, such as ZnO, CdSe, CdS, ZnS, etc.\textsuperscript{1-6} The principles of piezotronics can be applied to both of thin film and NWs, however, the NWs have better advantages than thin films for the following reasons. First, NWs have much larger surface area than thin films, so it can provide much more active positions than thin films. Second, NWs like ZnO NW can be synthesized using a hydrothermal approach at low temperature (lower than 100 °C) on any substrate with any shape and size, but it is difficult to grow high quality single crystal thin films on any substrate at low temperature. Third, NWs exhibit extremely and unique characteristics such as much higher elasticity, toughness and robustness than that of thin films which is easy to crack or fracture even under small strain. Fourth, it is possible to grow NWs with higher piezoelectric coefficient than thin film.\textsuperscript{7} Therefore, three-dimensional nanowire arrays are ideal for piezotronics and piezo-phototronics because they can bear a larger mechanical strain than thin film. In this thesis, ZnO and CdSe NW arrays are used as piezoelectric materials.

2.2 Zinc Oxide Nanowire Array

Zinc oxide (ZnO) is a versatile functional II-VI semiconductor and has been widely used in electronics, optics and photonics owing to its unique physical and chemical properties. The direct wide band-gap (3.37 eV) nature of ZnO makes it suitable for short wavelength optoelectronic applications. The high exciton binding energy (60 meV) property guarantees
efficient excitonic emission at room temperature.$^{8,9}$ In addition, ZnO is also biocompatible, biodegradable and biosafe for medical and environmental. Here, in the last few decades, ZnO NW has received considerable interest with the rise of nanoscience and nanotechnology. ZnO NW has two main crystal structures: hexagonal wurtzite and cubic zinc blende. ZnO usually crystallizes in hexagonal wurtzite structure (space group $C6\text{mc}$) with lattice parameters $a = 0.3296$ and $c = 0.52064$ nm under general conditions.$^{10}$ The wurtzite structure of ZnO NW can be described as a number of alternating planes composed of tetrahedrally coordinated $\text{O}^{2-}$ and $\text{Zn}^{2+}$ stacked alternately along the c-axis as shown in Figure 2.1. The asymmetric wurtzite structure of ZnO NW results in piezoelectric property, which inherently generates a piezopotential inside ZnO NW once it is strained.

![Atomic structure model of wurtzite ZnO nanowire](image)

*Figure 2.1 Atomic structure model of wurtzite ZnO nanowire.*

Three-dimensional ZnO NW arrays used in this dissertation were synthesized by two different synthesis methods: hydrothermal method and chemical vapor deposition (CVD) method, which includes vapor-liquid-solid (VSL) and vapor-solid (VS).$^{8,11,12}$
2.2.1 Synthesis of ZnO Nanowire Array via Hydrothermal Method

Hydrothermal method is a type of solution phase synthesis, in which the growth process is carried out in a liquid solution. The hydrothermal method of growing ZnO nanostructures was first reported by Andres-Verges et al. However, it was hard to control the fabrication until Vayssieres et al successfully used this method to control the fabrication of ZnO NWs on glass and Si substrates by the thermal decomposition of methenamine and zinc nitrate.

In this section, a commercial GaN/sapphire was chosen as the substrate to grow ZnO NW arrays because the lower lattices mismatch between GaN and ZnO (~1.9%).

GaN/Al₂O₃ substrate was first ultrasonically cleaned with acetone, isopropyl alcohol (IPA), and deionized water in sequence, and dried under a nitrogen flow. The growth solution was prepared by dissolving Zinc nitrate hexahydrate (Zn(NO₃)₂•6H₂O) (25 mM) and hexamethylenetetramine (HMT) (25 mM) in deionized water. The substrate was placed upside down on the surface of the solution in a 50 mL beaker which was sealed and put into an oven and heated up to 80°C. The solution was refreshed once every three hours to maintain a constant growth rate. The reactions occurred following equations:

\[(\text{CH}_2)_6\text{N}_4 + 6\text{H}_2\text{O} \leftrightarrow 4\text{NH}_3(g) + 6\text{HCHO}(g) \quad (2.1)\]

\[\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad (2.2)\]

\[\text{Zn(NO}_3)_2 \leftrightarrow \text{Zn}^{2+} + 2\text{NO}_3^- \quad (2.3)\]

\[\text{Zn}^{2+} + 2\text{OH}^- \leftrightarrow \text{Zn(OH)}_2 \quad (2.4)\]

\[\text{Zn(OH)}_2 \leftrightarrow \text{ZnO(s)} + \text{H}_2\text{O} \quad (2.5)\]
Figure 2.2 Attachment of hexamine to the non-polar facets of the zincite crystal allows the growth of the crystal in the (0001) direction. (a) hexagonal ZnO crystal (b) possible attachment of hexamine on to the non-polar facets leaving the polar face exposed allowing further crystal growth along the c-direction. (Reproduced with permission from reference 11).

The role of HMT is to supply the hydroxyl ions. It can be easily hydrolyzed in water and gradually produces OH\(^-\) to drive the precipitation reaction (equation 2.1 and 2.2). In addition, HMT also acts as a buffer as the rate of its hydrolysis increases with decreasing pH and vice versa. It is reported that the rate of hydrolysis of HMT is independent of the reaction that creates ZnO demonstrating that HMT does act as a kinetic buffer. Its phase is thermodynamically less stable in oxide formation and will precipitate out faster. Besides, it was proposed that HMT, as a long chain polymer and a nonpolar chelating agent, will preferentially attach to the non-polar facets of the zincite crystal, resulting in cutting off the access of Zn\(^{2+}\) to the non-polar facets and leaving only the polar (0001) face for epitaxial growth. Therefore, HMT acts as a shape-inducing polymer surfactant as well. Error! Reference source not found. shows the mechanism of attachment of hexamine on the nonpolar facets.\(^{11}\) In the start growth stage, Zn (NO\(_3\))\(_2\) was
decomposed into Zn$^{2+}$ and NO$_3^-$ (equation 2.3). The pH and the concentration of Zn$^{2+}$ ions are correlative qualities. The Zn$^{2+}$ reacted with OH$^-$ to form more soluble Zn(OH)$_2$ complexes (equation 2.4). With the gradual increase in the pH and the decrease in the concentration of the Zn$^{2+}$ ions, Zn(OH)$_2$ complexes become thermodynamically unstable and the Zn(OH)$_2$ complexes precipitated on the substrate will dehydrate to form ZnO nanoparticles (equation 2.5). The equilibrium of these reactions can be controlled by adjusting the reaction parameters, such as precursor concentration, growth temperature and growth time. Generally, precursor concentration determines the ZnO nanowire density. Growth time and temperature control the ZnO nanowire length and morphology.

Figure 2.3 (a) Top-view and (b) cross-section view FESEM images of vertically aligned ZnO nanowire arrays.

Figure 2.3a and b present the top-view and cross-section view FESEM images of the ZnO NW arrays. The as grown ZnO NWs are with 100 ~ 300 nm diameters and around 5μm lengths. All of the nanowires are perpendicularly grown and normal to the GaN/Al$_2$O$_3$ substrate due to epitaxial growth mechanism.
2.2.2 Synthesis of ZnO Nanowire Array via Chemical Vapor Deposition Method

Compared to other growth methods, such as wet chemistry and hydrothermal methods, chemical vapor deposition has many advantages: (1) the high quality of the NW’s crystallinity is guaranteed due to the employment of high-temperature and high-vacuum deposition circumstances, (2) the vapor deposition process was typically used in the conventional thin film fabrication, therefore understanding of thin film growth methods can be adopted in order to understand NW growth behaviors, (3) the location, composition, dimension, and organization of the grown NWs can be controlled by modulation of catalysts, growth sites and precursors in the vapor deposition processes, (4) vapor deposition of NWs can be used to grow various materials owing to its broad range of vapor deposition conditions.  

Generally, the chemical vapor deposition mechanisms of ZnO NW arrays growth can be divided into two categories: vapor-liquid-solid with catalysts and vapor-solid without foreign catalysts. The VLS mechanism was first proposed by Wagner and Ellis in the 1960s to explain the growth of Si whiskers using Au as a catalyst, in which the Au acts as a preferred site for the deposition of vapor precursors to form a liquid alloy droplet. Duan et al. demonstrated a general VLS process for the synthesis of NW morphology from a wide variety of compound semiconductor compounds including binary III-V materials (GaAs, GaP, InAs and InP), ternary III-V compounds (GaAs/P, InAs/P), binary II-VI compounds (ZnS, ZnSe, CdS and CdSe) and the group I-V compound of SiGe in 2000. In 2004, Wang et al. fabricated vertically aligned ZnO NWs with hexagonal patterns in large size by combining a self-assembly masking technique with surface epitaxial confinement to control the size and length of NWs.
A typical VLS process contains four successive steps: (1) the vapor phase precursor transport, (2) the adsorption and desorption of vapor phase precursor at the catalyst surface, (3) target material diffusion and growth across the liquid alloy catalyst, and (4) precipitation and epitaxy of solid crystals to form the NW morphology. In this process, a proper metal catalyst is vital for NW fabrication. In the VSL process, the catalyst (alloy) is in a solid phase that displays a different sticking probability of precursor molecules, diffusivity of adatoms and phase transformation behavior of the solid alloy. The size of the catalysts determines the diameter of the NWs and the size distribution of the applied catalyst colloids also controls the size distribution of the NWs, as shown in Figure 2.44. The catalyst-determined size control requires minimized lateral growth along the NW side walls, where all of the crystal deposition should occur only at the catalyst-NW interface. The length of the NWs is controlled by the growth time under ideal growth conditions.

The fundamental thermodynamics of the catalyzed nucleation and growth of NWs is the super-saturation and phase separation of catalyst alloy droplets. The metal catalyst can be rationally chosen from the phase diagram by identifying metals in which the NW component elements are soluble in the liquid phase but do not form solid compounds more stable than the desired NW phase. For ZnO NWs growth via a VLS process, the commonly used catalyst is Au. The liquid droplet catalyst acts as a preferential site for absorption of gas phase reactant and the nucleation site for ZnO crystallization when the liquid alloy droplet is super-saturated. NW growth starts after the liquid alloy droplet becomes supersaturated in reactant materials (ZnO) and continues as long as the catalyst alloy remains in a liquid phase and the reactant is available. During growth, the catalyst droplet directs the NW’s growth direction and defines the diameter of the NW. Finally, the growth terminates when the temperature is below the eutectic
temperature of the catalyst alloy or the reactant is no longer available. As a result, a nanowire obtained from the VLS process typically has a solid catalyst nanoparticle at its tip with a diameter comparable to that of the connected NWs.

Figure 2.4 Schematic illustration of the growth of dimension-controlled NWs. (a) The size of catalysts for NW diameter control. (b) The growth time for NW length control.

Foreign catalyst-assisted VLS are extensively employed in ZnO NW growth to control the size, density and orientation of NWs, however, the catalysts contamination and the limited selection of morphologies are the main drawbacks of the foreign-metal-catalyzed growth of ZnO NWs. Alternatively, ZnO NWs can be synthesized without any foreign catalysts, which offers a high lattice purity, elimination of unintentional doping and avoiding the poisonous effect of
metal catalysts. ZnO NW growth without foreign catalysts is complicated and involves various
growth mechanisms. Dislocation-driven growth is a popular mechanism in which the
anisotropic NW growth is achieved by preferred deposition at the self-perpetuating spirals of
axial dislocations under low supersaturation. Recently, self-catalyzed growth of ZnO NWs on
indium-tin-oxide (ITO)-coated glass substrate was reported, where no foreign catalysts are
applied. It provides a new way to grow the ZnO NWs without foreign metal catalysts.

Another typical ZnO NW growth method without using foreign catalysts is vapor-solid
deposition. It is first reported by Pan et al. that the creation of the noncatalyst-synthesized
nanostructures via the thermal evaporation of oxide powers. The precursor Zn powders were
heated to a high temperature to be decomposed into Zn vapor and oxygen gas. The
recombination and deposition of Zn and oxygen in the low temperature area formed the ZnO
nanostructure on substrates without using any foreign catalyst. The growth mechanism is
considered a VS process, where the ZnO was directly produced by the solidification of the vapor
state because of the rapid temperature drop at the deposition region. Without the restriction and
contamination of metal catalysts, ZnO can be deposited along any possible facets when the vapor
phase is supersaturated. Different surface energies of substrates and distinct growth rates along
different crystal facets are believed to be the main reasons for the formation of the ZnO
nanostructure morphology.

In order to produce high-purity ZnO NW arrays and avoid the poisonous effect of foreign
catalysts, in this work, the ZnO NW arrays are grown on ITO-coated glass via foreign catalyst-
free VLS and VS methods.
2.2.2.1 ZnO NW Arrays Growth via VLS

The ITO-coated glass (CG801N, Delta Technologies LTD) was chosen as the substrate, and it was first cleaned by sonicating sequentially in acetone, isopropyl alcohol and deionized water, respectively. The purity Zn powders (99.9%, metals basis, Alfa Aesar) and the cleaned ITO glass was put in a horizontal two-zone tube furnace with a length of 70 cm and a diameter of 4 cm as shown in Figure 2.55. The Zn powders were placed in an alumina boat. This boat with Zn powders was inserted upstream in the center of the left heating zone. The cleaned glass substrate was then placed downstream in the center of the right heating zone. The whole system was then pumped for an hour and then purified by purity Ar gas. The Zn powders in the left zone and the substrate in the right zone were gradually heated up 900 °C and 550 °C at a rate of 10 °C/minute, respectively. The heating temperature profile is shown in Figure 2.66. A 300 sccm (standard cubic centimeters per minute) Argon gas was used during the growth process as a carrier gas in the reaction zone during thermal evaporation. A 40 sccm Oxygen was employed as the reactant gas which will react with Zn particles to form ZnO NW arrays. The reaction was maintained for 1 hour and then the furnace was cooled down naturally to room temperature. White material formed on the glass substrate after the evaporation process was completed.

Figure 2.5 Schematic of the set-up used for the growth of ZnO NW arrays by CVD method
Morphological observation of the as-grown ZnO NW arrays was carried out using a field emission scanning electron microscopy (FESEM) shown in Figure 2.77a. It displays that the ZnO NWs are randomly grown out with similar size and its surface is smooth. It is believed that the growth mechanism of ZnO NW arrays is the multi-prong root growth process in Figure 2.77b. The liquid droplet is the In-Zn alloy since the eutectic temperature of the In-Zn system is very low (143.5 °C), which causes Zn vapor to supply sufficient Zn to melt the surface of the ITO thin film. In multi-prong growth process, more than one NW grows from a single liquid alloy droplet, which makes NWs grow randomly. In this case, the radius of the NW $r_w$ is less than the radius of the droplet $r_p$, and $r_w$ is not determined directly by $r_p$ but must be related to other structural factors such as the curvature of the growth interface and lattice matching between the catalytic particle and the NW.

![Figure 2.6 The heating temperature profiles of the two-zone furnace.](image)
2.2.2 ZnO NW Arrays Growth via catalyst-free VS

In order to grow vertically aligned ZnO NW arrays with hexagonal structure in a large area, a catalyst-free VS method was used. The growth procedure of VS is same with the VLS procedure, and the only difference is that a 60 nm thick ZnO thin film was sputtered on a cleaned ITO glass as seed layer before it was placed into the furnace. The sputtered ZnO seed layer provides a wetting surface for the nucleation of the Zn droplets and ensures the c-axis growth of the ZnO NWs.
Figure 2.8(a) FESEM images of the as-grown ZnO NW array via VS. (b) Schematic diagram of the VS growth process of ZnO NW arrays. $R_{Zn}$ and $R_{O}$ represent the absorption rates of Zn atoms and O atoms in the Zn/ZnO$_X$ droplet, respectively.

Figure 2.8a shows the top-view FESEM images of the as-grown ZnO NW arrays via VS method. It can be seen that the ZnO NW arrays are perpendicularly grown out with hexagonal tip and the diameters are in the range of 100-120 nm. The possible growth mechanism of the NW arrays is schematically illustrated in Figure 2.8b. In general, the growth of ZnO NWs from the vapor phase will go through two possible steps: (1) the condensation of Zn vapor into the liquid phase: $\text{Zn} \ (g) \rightarrow \text{Zn} \ (l)$; and (2) the oxidation of Zn: $\text{Zn} \ (l) + \text{O}_2 \ (g) \rightarrow \text{ZnO} \ (s)$. If the first step is the rate-limiting step, the condensed Zn will immediately be oxidized by oxygen gas into ZnO, and it would be considered as a VS deposition process. At the beginning, the Zn vapor is transported along the Ar carrier gas flowing to the low temperature ($550 \ ^\circ C$) zone and condensed from vapor phase into liquid phase, and the Zn liquid droplet acts as the favorable sites for the absorption of Zn vapor and O$_2$ gas (region I of Figure 2.8b). Herein, $R_{Zn}$ and $R_{O}$ present the absorption rates of Zn atoms and O atoms, respectively. The oxygen flow rate is kept stable throughout the whole process, the $R_{O}$ can be considered as a constant. In the early stage of the reaction process, the pressure of the Zn vapor is relatively low, namely $R_{Zn} < R_{O}$, thus the Zn
liquid droplet will be immediately oxidized into ZnO as a nucleation site (region II of Figure 2.8b). As the reaction proceeds, the pressure of the Zn vapor increases gradually. When it increases to a certain level, \( R_{Zn} \) will be equal to or even larger than \( R_{O} \), resulting in the newly formed droplets. With the absorption of Zn and O, ZnO particles will epitaxially deposit at the interface of the Zn/ZnO\(_x\) droplets and the ZnO substrate. ZnO NWs with the same sizes as the droplets will start to grow. If the condition \( R_{Zn} \geq R_{O} \) is satisfied during a period of time with the stable pressure of the Zn vapor maintained, the NWs will grow continuously with the Zn/ZnO\(_x\) droplets (region III of Figure 2.8b). When the pressure of the Zn vapor decreases, the condition will change to \( R_{Zn} < R_{O} \). Under this condition, the Zn/ZnO\(_x\) droplets will be depleted gradually (region IV of Figure 2.8b), and the growth of the NWs will follow a VS mechanism.\(^{25}\) It should be noted that increasing the oxygen flow rate will accelerate the oxidation of the Zn powders and result in a lower Zn vapor supersaturation. Thus, the large oxygen flow rates (40 sccm in this experiment) will accelerate the depletion of the catalytic Zn/ZnO\(_x\) droplets and make the growth of NWs follow a VS mechanism, which will more readily promote thickness of the NWs due to the possible transverse growth.\(^{26}\) In addition, the ZnO NWs in the FESEM image of Figure 2.8a obviously coalesced together at the top, which is the result of the VS transverse growth.

### 2.2.3 Characterization of ZnO Nanowire Array

The transmission electron microscope (TEM) image (Figure 2.9 a) of a single ZnO NW with corresponding (Figure 2.9b) indexed selected area electron diffraction (SAED) pattern demonstrate that ZnO NW is single crystal with wurtzite structure and grows along \( c \)-axis. In order to confirm the element composition of ZnO NWs, an energy dispersive spectroscopy (EDS) spectrum (Figure 2.9c) was measured. The EDS spectrum of a single ZnO NW reveals the existence of zinc and oxygen, and the EDS peaks of carbon and copper come from TEM sample
holder and grid. To further investigate the crystallinity and crystal phase of the pristine ZnO NWs, XRD spectrum was recorded and exhibited in Figure 2.9d. The XRD spectrum of the pristine ZnO NWs exhibits a typical XRD pattern for the ZnO NWs with high-purity wurtzite hexagonal phase where a strong and sharp diffraction peak and several relative weak peaks appear at around 34.4°, 47.5°, 56.6°, 62.8° and 69.1°, respectively, representing (002), (102), (110), (103) and (201) planes of the hexagonal structure, which match well with standard hexagonal ZnO (JCPDS CARD No. 36-1451).

Figure 2.9 (a) TEM image of a single ZnO NW with corresponding (b) SAED pattern and (c) EDS spectrum. (d) XRD pattern of pristine ZnO NW arrays.
2.3 Cadmium Selenide Nanowire Array

As one of the most important II-VI group semiconductors, cadmium selenide (CdSe) have been used in a wide range of applications, such as thin-film transistors,\textsuperscript{27} light-emitting diodes,\textsuperscript{28} photovoltaic cells,\textsuperscript{29} optical memories,\textsuperscript{30,31} sensors\textsuperscript{32} and biomedical imaging\textsuperscript{33}, because of its distinct nonlinear optical properties, luminescent properties, quantum-size effect and the narrow band gap in visible light range. Recently, CdSe NWs have been significantly studied in
the optoelectronic field due to its unique opto-electrical properties, a high aspect ratio and surface to volume ration. Moreover, CdSe NW is a wurtzite structure crystal with non-central symmetry, a piezopotential can be generated in CdSe NW by applying an external stress because of the polarization of ions.\textsuperscript{1} This piezopotential has a strong effect on the charge carrier transport at the interface/junction due to the simultaneous possession of piezoelectricity and semiconductor properties, which is the fundamental principle of piezotronic and piezophototronic effects. Therefore, piezoelectric CdSe NWs are used to improve the performance of optoelectronic devices, such as photodetectors, photocells, solar cells and LEDs.\textsuperscript{5}

The most table crystal structure for CdSe is wurtzite structure with hexagonal unit cells (space group $P6_3mc$). The structure of CdSe can be simply defined as a number of alternating planes, which are composed of tetrahedrally coordinated Se$^{2-}$ and Cd$^{2+}$ ions, stacked alternatively along the $c$-axis as shown in Figure 2.10a. The red and gray balls present the Cd$^{2+}$ cations and Se$^{2-}$ anions, respectively. This structure is composed of repeating tetrahedral units, where the Cd$^{2+}$ cations are located in the center while the Se$^{2-}$ anions are on the corners. The tetrahedral coordination in CdSe results in non-central symmetric structure and thus piezoelectricity. The positive and negative charge centers overlap under strain-free situations. Once a stress is applied along the $c$-axis, the overlapped positive and negative charge centers are relatively displaced, resulting in a dipole moment along the $c$-axis. All the dipole moments along the NW can create a macroscopic piezopotential, as shown in Figure 2.10 b and c. The magnitude of the piezopotential depends on the deformation of the crystal, and the dielectric constant. Figure 2.10 b and c are the distribution of the piezopotential along a doping free CdSe NW under different stresses by the Lippman theory. Figure 2.10b presents the piezopotential distribution when a lateral stress of 80 nN is employed on the top end of NW and the bottom end is fixed and electrically grounded.
When the lateral stress is applied, CdSe NW is bent. The tensile side shows a positive potential while the compressive side exhibits a negative potential with the same absolute value. Figure 2.10c illustrates the piezopotential distribution when the NW is compressed by a stress. The top of the NW presents a negative potential and the bottom of the NW shows a positive potential with the same amplitude. The amplitude of the negative potential rises as the strain increases because of further separation of the positive and negative charge centers in the crystal.

2.3.1 Synthesis of CdSe Nanowire Array

One dimensional CdSe nanostructures can be grown by different techniques, such as thermal evaporation, pulsed laser deposition, chemical electrodeposition and hydrothermal methods. Among of all these routes, chemical vapor deposition is the most commonly used technique to grow CdSe NWs. In this section, CdSe NW arrays were synthesized on muscovite mica substrate via an Au-catalyzed vapor-liquid-solid growth process.

The schematic of the fabrication procedure of CdSe NW arrays is shown in Figure 2.11. First, a freshly cleaved muscovite mica substrate (SPI, grade V-5 research quality) was loaded into an electron beam evaporation system (Kurt J. Lesker, PVD75) for CdSe seed layer deposition. After being coated with 100 nm CdSe thin film, the mica substrate was transferred to a sputtering system (Cressington coating system, 308R) for gold catalyst deposition. The thickness of the Au catalyst was 0.8 nm. CdSe powders (Alfa Aesar, 99.999% purity, metal basis) were loaded in the alumina crucible as the evaporation material source. The growth was carried out in a typical thermal evaporation horizontal tube furnace where the CdSe powders were positioned in the center of the furnace and the mica substrate was sited downstream to collect CdSe. The furnace was then heated to 750 °C and 160 sccm H₂/Ar (8%/92%) gases were introduced and the whole system was maintained at atmospheric pressure. The samples were
taken out for characterizations after the experiment completed and the system was cooled to room temperature.

**Figure 2.11 Schematic of the synthesis procedure of CdSe NW arrays.**

### 2.3.2 Characterization of CdSe Nanowire Array

The as-grown CdSe NW arrays were characterized by using a LEO 1530 field emission scanning electron microscope (FESEM) system and a JEOL 2010 TEM equipped EDS. Figure 2.12a and b are the top-view and tilt-view FESEM images of the as-grown CdSe NW arrays. It can be seen that CdSe NW arrays grow vertically in a large-area and are separately aligned normal to the substrate. The density of the NWs is calculated as 5~6 NWs per µm². The high magnification inset images show NWs have several micrometers in length and 150-200 nm in diameter and each NW is terminated with a spherical or semi-spherical Au particles on the tip, which illuminates the CdSe NW growth is governed by the typical catalyst-assisted VLS growth mechanism. TEM image and the corresponding SAED pattern of a single CdSe NW are presented in Figure 2.12c and d, which indicate CdSe have a preferential growth direction along [0002] direction, and the Au particle is located on the top of the NW.
Figure 2.12 (a) Top-view and (b) tilt-view FESEM images of CdSe NW arrays. (c) Low magnification TEM image of a single CdSe NW with corresponding (d) SAED pattern.

XRD patterns of mica substrate and mica with CdSe NW array are shown in Figure 2.13a. The muscovite mica substrate shows several strong peaks which can be identified as (004), (006), (008), (0010), (0012) and (0014), indicating the highly crystallinity of the substrate. In contrast, only two additional diffraction peaks (002 and 004) can be observed from the XRD pattern of the as-grown CdSe NW array on mica, which illuminates the CdSe NWs are single crystal and grow along c-axis. The EDS spectrum of a single CdSe NW in Figure 2.13b displays several strong peaks of Cd and Se, representing the existence of Cd and Se elements. The EDS peaks of carbon and copper come from TEM sample holder and grid.
2.4 Conclusion

In summary, ZnO NW arrays have been synthesized on different substrates via hydrothermal method and CVD methods. The growth mechanisms have been discussed and compared. Vertically aligned ZnO NW arrays have been achieved on GaN/sapphire substrate through hydrothermal method and ZnO-coated ITO glass through VS method. In contrast, ZnO NW arrays grown directly on ITO glass exhibited random orientation via VLS method. Their morphologies and structures have been investigated by comprehensive characterizations. In addition, CdSe NW array has been synthesized on mica substrate through CVD method. The vertically grown CdSe NW array exhibits a well alignment. The structural characterization, element composition, crystallinity and crystal phase of the as-grown CdSe NW have been studied through using FESEM, TEM, EDS and XRD.
Reference


Chapter 3 Self-Powered Active Gas Sensors Based on Piezotronic Effect

3.1 Introduction

A gas sensor is defined as a device which can detect the presence of gases in an area based on interaction between its sensing part and target gases.\(^1\) As one of the most important electronic devices, it has been studied and used for long time since the first gas sensor based on platinum wire was commercialized in 1923.\(^2\) Following extensive demand for better gas sensors, the first semiconductor gas sensor was reported in 1962.\(^3\) After that, the gas sensors based on semiconductors have been widely investigated and made enormous progress in the last decades. Currently, gas sensors based on semiconductor, especially semiconducting metal oxide materials, are becoming increasingly important and are widely utilized in the fields of environmental monitoring, public security, automotive application, food industry, etc.\(^4\)–\(^8\) The semiconducting metal oxides are usually extremely sensitive to chemical changes in atmosphere due to their electronic, chemical and physical properties. Furthermore, they possess several specific advantages: low cost, easy fabrication, flexibility in production, simplicity of use, etc.\(^9,10\) In the early period, metal oxide semiconductor gas sensors were often fabricated in the form of thin film. However, theses thin film sensors have some disadvantages, such as poor sensitivity at low gas pressures, unstable operation, nonlinear responses, etc., owing to their overheating working temperature and limited surface-to-volume ratios.\(^1,2,11,12\) With the development of nanotechnologies, nanostructured metal oxide semiconductors (e.g. nanowires, nanoparticles, nanobelts) have gained much more attention for their applications in highly sensitive and selective gas sensors at room temperature because of their high surface-to-volume ratio, huge surface area and availability of versatile structures.\(^6,8,13,14\)
With the rapid progress of mobile technology, high-speed wireless network and geographical positioning system (GPS), the massively distributed environment monitoring system becomes possible, which requires the gas sensors to have small size and extremely low power consumption, even self-powered system.\(^{15,16}\) These requirements motivate scientists to work hard in the development of self-powered active high performance gas sensors. The application of piezoelectric semiconductor nanomaterials is able to meet these demands. In order to power nanodevices and nanosystems, nanogenerators based on piezoelectric semiconductor NWs, such as ZnO, CdS, CdSe, etc., have been proposed which can convert mechanical energy into electrical energy due to their unique piezoelectricity and semiconductor properties.\(^{6-8}\)

Recently, a self-powered device, named as an active gas sensor,\(^{10-15}\) has been fabricated by combining nanogenerator with gas sensor. This new type of self-powered active gas sensor uses the output voltage from the nanogenerator, which is created by the strain-induced ionic polarization in the piezoelectric semiconducting crystal as either a power source or sensing signal in response to different gases. This new piezopotential-driven sensing mechanism opens a new way for the next generation of gas sensors and expands the scope of applications for self-powered nanosystems.\(^{12,16}\)

In the following sections, two different kinds of piezoelectric semiconductors were used as self-powered active gas sensors. First one was ZnO NW array grown through hydrothermal method, and second one was well-aligned CdSe NW array synthesized through CVD method.

### 3.2 Self-Powered Gas Sensors Based on ZnO/Metal Oxide Core/Shell Nanowire Arrays

As one of the most commonly used piezoelectric semiconductor materials, ZnO NWs have been broadly utilized for nanogenerators and nanogenerator-based active sensors due to its
unique physical and chemical properties. For instance, ZnO NWs-based active photodetectors have been reported in 2012, the output piezoelectric voltage was generated inside ZnO NWs under different intensities of UV light illumination. Likewise, self-powered ZnO NWs-based active gas sensors have also been proposed. For self-powered gas sensors, the free charge carrier density inside ZnO NW can be influenced by reducing or oxidizing gas molecules which are adsorbed on the surface of NW. Moreover, the piezoelectric output of ZnO NW can be modified by the free charge carriers inside NW, therefore the piezoelectric output of ZnO NW will be influenced by the target gas. In this way, the piezoelectric output of ZnO NW under applied stress works not only as a power source but also as a response signal to the target gas. In other hand, surface modification and heterostructure, such as noble metal-decorated NW, core/shell structure, p-n junction, have been reported as an effective strategy for traditional metal oxide semiconductor gas sensors to enhance the sensing performance of gas sensors. Based on this concept, several self-powered gas sensors based on ZnO NWs were studied, such as Pt/ZnO NWs self-powered gas sensor, CuO/ZnO p-n junction self-powered gas sensor, etc. In this part, ZnO/SnO$_2$, ZnO/In$_2$O$_3$ and ZnO/WO$_3$ core/shell NW arrays have been fabricated to make self-powered active gas sensors. The heterostructures can adjust the free-carrier density of ZnO NWs, thus strongly affect the piezoelectric output of the devices.

### 3.2.1 Synthesis and Characterization of ZnO/Metal Oxide Nanowire Arrays

ZnO NW arrays were grown on GaN/Al$_2$O$_3$ substrate through the hydrothermal method as mentioned in Chapter 2. In brief, the cleaned 2 × 2 cm$^2$ GaN/Al$_2$O$_3$ substrate was placed face-down in the precursor solution which was prepared by dissolving Zinc nitrate hexahydrate (25 mM) and hexamethylenetetramine (HMT) (25 mM) in deionized water. The solution was sealed and heated up to 80°C for 12 hours. The as-grown ZnO NW array has a ~5µm long as shown in
Figure 2.3 in Chapter 2, which is long enough in this experiment to avoid a short circuit between the top and bottom electrodes.

Vacuum magnetron sputtering deposition was chosen for shell layer coating because coating under vacuum condition can reduce unnecessary contamination and impurities, and the argon gas can promote the diffusion of deposition species and increase the homogeneity of the surface coatings. In addition, surface coating on ZnO usually form a polycrystalline structure induced by the large lattice mismatch of ZnO compared to other metal oxide materials. The grain boundaries and rough surface of the polycrystalline coating may essentially increase the sensing performance of the NWs.

After ZnO NW array synthesis, it was loaded in a Lesker PVD75 system to coat the surface coatings. Shell layers with 50 nm thickness of SnO$_2$, In$_2$O$_3$ and WO$_3$ were sputtered on the ZnO NW arrays with a deposition rate range of 0.2-0.5 Angstrom/s at room temperature, respectively. Figure 3.1 shows the FESEM images and the corresponding EDS spectra of ZnO/SnO$_2$, ZnO/In$_2$O$_3$ and ZnO/WO$_3$. It can be found that the ZnO NWs were fully covered by the shell layers of SnO$_2$, In$_2$O$_3$ and WO$_3$, and the element peaks in the corresponding EDS spectra further confirmed coating success.
3.2.2 Gas Sensor Fabrication and Measurement Process

Figure 3.2 is the schematic of the fabrication process of ZnO/metal oxide core/shell NW array self-powered active gas sensors. After shell layer coating, the core/shell NWs were placed in a cressington 308 R system to deposit bottom electrode. A gold layer with 100 nm thickness
was sputtered on the corner of the substrate as bottom electrode, and a 100 nm-thick Pt thin layer was sputtered on a polyester film with a groove density of 1000 grooves/mm (Edmund Optics) as a top electrode. The flexible polyester film was used to enhance the effective contact between the top electrode and NWs because the flexibility of the polyester film can guarantee to follow the height profiles of NWs even NWs had moderate alignment and slight height difference. The Pt-coated polyester film was then placed on top of the NWs and the top and bottom electrodes were connected to measurement equipment with lead wires. Finally, the whole device was packaged by Kapton film which further provides a solid contact between NWs and top electrode.

![Figure 3.2 Schematic of gas sensor fabrication based on core/shell NW arrays.](image-url)
Figure 3.3 is the homemade gas sensor testing platform. The whole testing system is fixed on an electrical testing board. The testing system includes three parts: testing chamber, gas inlet and outlet. The testing chamber is sealed by a flexible and elastic layer of Polydimethylsiloxane (PDMS) (Dow Corning Sylgard 184 silicone elastomer), and will be covered by aluminum foil to block light during testing. The testing gases are injected into the sealed chamber from gas inset by syringe. The gas outlet is connected to a vacuum pump for purging the chamber and gas sensor. The top and bottom electrodes of gas sensors are connected to the Sourcemeter keithley 2400 which is connected to a computer. The electrical signal is continuously monitored during the whole procedure.

The tested gases in this part are NO₂ and H₂S. The initial concentrations for NO₂ and H₂S gases are 2% diluted by N₂. All these initial gases will be diluted by using 1 L sealed plastic bags. The volume of the chamber is around 50 mL. Table 3.1 indicates the gas dilution process from initial 2% to desired concentrations.
Table 3.1  Dilation process of 2% initial gas. (Chamber size: 50 mL)

<table>
<thead>
<tr>
<th>Initial concentration</th>
<th>Process</th>
<th>Pre-diluted concentration</th>
<th>Process</th>
<th>Final concentration in Chamber</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%</td>
<td></td>
<td></td>
<td>Inject 2.5 mL of 2% gas into chamber</td>
<td>1000 ppm</td>
</tr>
<tr>
<td>2%</td>
<td>Inject 10 mL of 2% gas into 1L bag</td>
<td>200 ppm</td>
<td>Inject 0.5 mL of 200 ppm gas into chamber</td>
<td>2 ppm</td>
</tr>
<tr>
<td>200 ppm</td>
<td></td>
<td></td>
<td>Inject 0.25 mL of 200 ppm gas into chamber</td>
<td>1 ppm</td>
</tr>
<tr>
<td>200 ppm</td>
<td>Inject 10 mL of 200 ppm gas into 1L bag</td>
<td>2 ppm</td>
<td>Inject 12.5 mL of 2 ppm gas into chamber</td>
<td>500 ppb</td>
</tr>
<tr>
<td>2 ppm</td>
<td></td>
<td></td>
<td>Inject 5 mL of 2 ppm gas into chamber</td>
<td>200 ppb</td>
</tr>
<tr>
<td>2 ppm</td>
<td></td>
<td></td>
<td>Inject 2.5 mL of 2 ppm gas into chamber</td>
<td>100 ppb</td>
</tr>
<tr>
<td>2 ppm</td>
<td></td>
<td></td>
<td>Inject 1.25 mL of 2 ppm gas into chamber</td>
<td>50 ppb</td>
</tr>
<tr>
<td>2 ppm</td>
<td></td>
<td></td>
<td>Inject 0.5 mL of 2 ppm gas into chamber</td>
<td>20 ppb</td>
</tr>
</tbody>
</table>
3.2.3 Results and Discussion

All the core/shell gas sensors were first used as a traditional gas sensor to detect different concentrations of NO$_2$ and H$_2$S at 1.5 V bias. Figure 3.4 The sensitivities of gas sensors based on ZnO/SnO$_2$, ZnO/In$_2$O$_3$ and ZnO/WO$_3$ core/shell NW arrays responding to (a) NO$_2$ and (b) H$_2$S gases. Sensitivity (S) is one of the important parameters of the gas sensor, which can be defined as:

$$S = \frac{I_{gas} - I_{air}}{I_{air}} \times 100\%$$  \hspace{1cm} (3.1)

Where S is the sensitivity, $I_{gas}$ is the output current of the gas sensor when it is exposed to target gas, and $I_{air}$ is the current of the sensor in air. It can be observed that all the gas sensors can detect the ppb (parts per billion) level NO$_2$ and H$_2$S. The ZnO/In$_2$O$_3$ gas sensor has the best sensitivity to NO$_2$ and H$_2$S gases owing to the intrinsic properties of the sensing materials.

Figure 3.4 The sensitivities of gas sensors based on ZnO/SnO$_2$, ZnO/In$_2$O$_3$ and ZnO/WO$_3$ core/shell NW arrays responding to (a) NO$_2$ and (b) H$_2$S gases.
All the gas sensors based on ZnO/SnO$_2$, ZnO/In$_2$O$_3$ and ZnO/WO$_3$ NW arrays were then measured at 0 V bias in dry air, 1000 ppm (parts-per-million, $10^{-6}$) NO$_2$ and 1000 ppm H$_2$S at room temperature. A 0.2 N compressive stress was repeatedly applied on the gas sensor during measurement process. The piezoelectric output voltages of ZnO/SnO$_2$ NW array gas sensor are summarized in Figure 3.5. It can be observed that an average output voltage of ~60 mV was detected when ZnO/SnO$_2$ NW array gas sensor was measured in dry air under a 0.2 N repeated stress without any power supplied. After 1000 ppm NO$_2$ was injected into the chamber, the average output voltage was increased from ~60 mV to ~140 mV, while, after 1000 ppm H$_2$S was injected into the chamber, the average output voltage was decreased from ~140 mV to ~20 mV.

![Figure 3.5 Piezoelectric output voltages of ZnO/SnO$_2$ NW array gas sensor in (a) dry air, (b) 1000 ppm NO$_2$ and (c) 1000 ppm H$_2$S under repeatedly compressive stress at room temperature.](image)

The self-powered sensing mechanism of the ZnO/SnO$_2$ NW arrays gas sensor is shown in Figure 3.6. The ZnO/SnO$_2$ NWs have two functions: one is an energy supply since the ZnO NWs can produce piezoelectric output power under deformation; the second is a gas sensor because the piezoelectric output of ZnO NWs will be influenced by the tested gases. When the sensor is placed in air without any compressive force (Figure 3.6a), the device is in the natural state without any piezoelectric output. Besides, oxygen ions ($O^-$) are adsorbed (equation $O_2 + 2e \rightarrow$...
at the SnO$_2$ nanograin boundaries and the interface of SnO$_2$ and ZnO grains, contributing to the enhancement of the surface reactions between adsorbed oxygen and current-carrying electrons.

Figure 3.6 The working mechanism of the self-powered ZnO/SnO$_2$ NW arrays gas sensor.

ZnO and SnO$_2$ are n-type semiconductors and the electron affinity ($\chi$) of ZnO and SnO$_2$ are -4.3 and -4.5 eV, respectively. The direct band gaps of ZnO and SnO$_2$ are 3.4 and 3.6 eV, respectively. The Fermi energy level of SnO$_2$ is higher than that of ZnO, which is caused by the different work functions between them. When the SnO$_2$ contact with ZnO, electrons will flow
from $\text{SnO}_2$ into ZnO until the Fermi level on each side reached a new equilibrium. The n-n heterojunction is formed at the interface between ZnO and SnO$_2$, interface with a depletion layer building up on the SnO$_2$ side and an accumulation layer building up on the ZnO side. When a compressive stress is applied on the sensor (Figure 3.6b), a piezoelectric field is created along ZnO NWs, which will drive the free electrons flowing from the top end of NWs to the bottom end of NWs. The free electron density of ZnO NWs is low, thus the screening effect is weak, resulting in a high piezoelectric output voltage (Figure 3.6c). When the gas sensor is exposed to oxidizing gas, herein is NO$_2$, at room temperature without any applied force (Figure 3.6d), NO$_2$ will also be adsorbed ($\text{NO}_2 + e \rightarrow \text{NO}_2^-$) at the SnO$_2$/SnO$_2$ nanograin boundaries and the interface of SnO$_2$ and ZnO grains. The adsorbed NO$_2$ further reduces the free electron density of the ZnO NWs. When a compressive force is applied on the sensor (Figure 3.6e), a similar piezoelectric field is created along ZnO NWs. the lower free-electron density inside ZnO NWs makes the screening effect weaker, resulting in a larger piezoelectric output voltage(Figure 3.6f). When the gas sensor is exposed to reducing gas, herein is H$_2$S, at room temperature without any applied force (Figure 3.6g), H$_2$S will react with the adsorbed oxygen and NO$_2$ ions (equation $H_2S + 3O^- \rightarrow H_2O + SO_2 + 3e$) to release the trapped electrons back to the NWs, resulting in an increment of the free electron density of ZnO NWs. When a compressive force is applied on the sensor (Figure 3.6h), the strain-induced piezoelectric potential is strongly screened by more free electrons, resulting in a smaller output voltage (Figure 3.6i).
\[ O_2 + 2e \rightarrow 2O^- \]  
(3.2)

\[ NO_2 + e \rightarrow NO_2^- \]  
(3.3)

\[ H_2S + 3O^- \rightarrow H_2O + SO_2 + 3e \]  
(3.4)

The ZnO/In$_2$O$_3$ and ZnO/WO$_3$ gas sensors were also measured without external power source under the similar procedure. The output voltages of ZnO/SnO$_2$, ZnO/In$_2$O$_3$, and ZnO/WO$_3$ gas sensors in air, 1000 ppm NO$_2$ and 1000 ppm H$_2$S at room temperature are displayed in Figure 3.7 and Figure 3.8, respectively. It can be found that both of the ZnO/In$_2$O$_3$ and ZnO/WO$_3$ gas sensors have the similar trend with the ZnO/SnO$_2$ gas sensor, namely the output voltage will become larger when exposed to oxidizing gas (NO$_2$), but smaller when exposed to reducing gas (H$_2$S) because they are all n-type semiconductors and have the similar structure, though their output voltages are different even under the same conditions due to the intrinsic properties of the sensing materials.

![Piezoelectric output voltages of ZnO/In$_2$O$_3$ gas sensor](image)

*Figure 3.7 Piezoelectric output voltages of ZnO/In$_2$O$_3$ gas sensor in (a) dry air, (b) 1000 ppm NO$_2$ and (c) 1000 ppm H$_2$S under repeatedly compressive stress at room temperature.*
3.2.4 Conclusion

The gas sensors based on ZnO/SnO₂, ZnO/In₂O₃ and ZnO/WO₃ core/shell heterostructure NW arrays have been fabricated. All the sensors could be used to detect oxidizing gas and reducing gas without any power supply. The self-powered behavior comes from the strain-induced ionic polarization in ZnO NWs, which was used as not only the power source but also the sensing part.

3.3 Self-Powered CdSe Nanowire Array Sensor

II-VI group semiconductor nanomaterials with wurtzite structure have attracted much interest as building blocks for future self-powered nanosystems since a piezoelectric potential can be created in the crystal when a stress is applied. This piezopotential can be used to convert mechanical energy into electrical energy or develop novel electronic devices with much enhanced performance through controlling the transport behavior of charge carriers, which is called piezotronic effect. In the last decade, ZnO nanostructures have been significantly studied on the piezotronic-related applications. As one of the commonly used II-VI semiconductors, CdSe nanostructures (such as thin film, quantum dots) have been broadly used for applications,
such as light-emitting devices, photovoltaics, nanosensors, gas sensor, etc.,\textsuperscript{21–26} due to its unique chemical and physical properties. Recently, CdSe NW has been studied as an attractive potential candidate to replace ZnO NWs in energy harvesting and piezo-phototronic devices. However, there are only a few reports on CdSe NWs as piezoelectric materials. In addition, CdSe nanostructures have been used as selective chemical gas nanosensors for the gas detection, such as oxygen,\textsuperscript{27} carbon dioxide,\textsuperscript{28} ethanol,\textsuperscript{29} etc., owing to their fluorescence quenching properties and unique structures. In the next section, a self-powered CdSe NW array gas sensor is proposed.

3.3.1 Gas Sensor Fabrication and Measurement Process

CdSe NW array was synthesized on muscovite mica substrate via CVD method as described in Chapter 2. Briefly, the freshly cleaved muscovite mica substrate was first coated with a 100 nm-thick CdSe seed layer via electron-beam evaporation deposition and then sputtered a 0.8 nm-thick Au catalyst thin film via magnetron sputtering deposition. The as-coated substrate was loaded into a furnace to grow CdSe NW array via a CVD method.

![Figure 3.9 Schematic of gas sensor fabrication based on CdSe NW array.](image-url)
(PMMA) layer with ~2 µm thickness was first spin-coated on the as-grown CdSe NW array to provide extra support for NWs and avoid a possible top-bottom electrode short circuit. The PMMA layer was then placed into a compact tabletop low temperature plasma etching system (Plasma Prep II) to etch the extra PMMA layer and make sure the tips of CdSe NWs weren’t covered by PMMA. Finally, a thin layer of platinum (~100 nm) was sputtered on a polyester film with a groove density of 1000 grooves/mm (Edmund Optics) as a top electrode. The top electrode was integrated to the CdSe NW array and the whole device was packaged by Kapton film. The gas sensor is measured inside the homemade gas sensor testing platform (Figure 3.3).

*Table 3.2* Dilution process of 2% initial gas. *(Chamber size: 50 mL)*

<table>
<thead>
<tr>
<th>Initial concentration</th>
<th>Process</th>
<th>Pre-diluted concentration</th>
<th>Process</th>
<th>Final concentration in Chamber</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%</td>
<td></td>
<td></td>
<td>Inject 2.5 mL of 2% gas into chamber</td>
<td>1000 ppm</td>
</tr>
<tr>
<td>2%</td>
<td>Inject 100 mL of 2% gas into 1L bag</td>
<td>2000 ppm</td>
<td>Inject 2.5 mL of 2000 ppm gas into chamber</td>
<td>100 ppm</td>
</tr>
<tr>
<td>2000 ppm</td>
<td></td>
<td></td>
<td>Inject 1.25 mL of 2000 ppm gas into chamber</td>
<td>50 ppm</td>
</tr>
<tr>
<td>2000 ppm</td>
<td>Inject 100 mL of</td>
<td>200 ppm</td>
<td>Inject 2.5 mL of</td>
<td>10 ppm</td>
</tr>
</tbody>
</table>
The tested gases in this part are NO$_2$ and NH$_3$. The initial concentrations of the gases are 2% diluted by N$_2$. All these initial gases will be diluted by using 1 L sealed plastic bags. The volume of the chamber is around 50 mL. Table 3.2 indicates the gas dilution process from initial 2% to desired concentrations.

### 3.3.2 Results and Discussion

![Graphs](image)

*Figure 3.10 The sensitivity of CdSe NW array gas sensor responding to (a) NO$_2$ and (b) NH$_3$ gases*

First, the CdSe NW array gas sensor was measured as a traditional gas sensor under different concentrations of NO$_2$ and NH$_3$ at 1.5 V bias. Figure 3.10 The sensitivity of CdSe NW array gas sensor responding to (a) NO$_2$ and (b) NH$_3$ gases It can be seen that the CdSe NW array gas sensor can detect ppm level of NO$_2$ and NH$_3$, though the sensitivity is lower than that of gas sensors based on metal oxide semiconductors. The mechanism of CdSe NW array gas sensor is
also based on oxygen-adsorption theory. CdSe is an n-type semiconductor, and its electronic conduction originates from point defects, which suggests Se vacancies or foreign atoms that act as donors or acceptors. In the dry air, CdSe NWs are expected to adsorb oxygen. The adsorbed $O^-$ traps electrons from the conduction band of CdSe NWs as shown in equation $O_2 + 2e \rightarrow 2O^-$

\[ (3.2) \]

inducing the formation of a depletion layer on the surface of the CdSe NWs. When it is exposed to oxidizing NO$_2$ gas, NO$_2$ molecules are also adsorbed at the active sites on the surface of the CdSe nanocrystals ($NO_2 + e \rightarrow NO_2^-$

\[ (3.3) \]

resulting in the free electrons inside CdSe NW decrease. When it is exposed to reducing gas of NH$_3$, the adsorbed oxygen ions on CdSe NWs will take part in the oxidation of NH$_3$. The oxygen ions on the surface of NWs will react with the NH$_3$ molecules ($2NH_3 + 3O^- \rightarrow 3H_2O + N_2 + 3e$

\[ (3.5) \]) and the electrons are released back to the conduction band of CdSe NWs.

\[ 2NH_3 + 3O^- \rightarrow 3H_2O + N_2 + 3e \]  

\[ (3.5) \]

---

**Figure 3.11** Piezoelectric output voltages of CdSe gas sensor in (a) dry air, (b) 1000 ppm NO$_2$ and (c) 1000 ppm NH$_3$ under repeatedly compressive stress at room temperature.
The CdSe NW array gas sensor was then tested at 0 V bias in dry air, 1000 ppm NO₂ and 1000 ppm NH₃ at room temperature. Figure 3.11 is the summary of piezoelectric output voltages of CdSe gas sensor in dry air, 1000 ppm NO₂ and 1000 ppm NH₃ under repeatedly compressive stress at room temperature. It can be found that an average output voltage of ~40 mV was gained when CdSe NW array gas sensor was tested in dry air under a 0.2 N repeated stress without any power supplied (Figure 3.11a). After 1000 ppm oxidizing gas of NO₂ was injected into the chamber, the average output voltage was increased from ~40 mV to ~85 mV (Figure 3.11b), while, after 1000 ppm reducing gas of NH₃ was injected into the chamber, the average output voltage was decreased from ~85 mV to ~20 mV (Figure 3.11c). The working principle of its self-powered behavior is similar with ZnO-based gas sensors. Briefly, when the sensor was compressed repeatedly in air, a relative high piezoelectric output voltage can be created due to the piezoelectricity of CdSe NWs (Figure 3.11a). When it is exposed to oxidizing gas, the adsorbed NO₂ molecules further reduces the free electron density of the CdSe NWs, resulting in a weaker screening effect, and thus higher piezoelectric output voltage (Figure 3.11b). When reducing gas is introduced, the NH₃ will react the adsorbed oxygen and NO₂ ions (equation $H_2S + 3O^- \rightarrow H_2O + SO_2 + 3e$ (3.4) to release the trapped electrons back to the NWs, resulting in the free electron density of CdSe NWs increases, which will create a stronger screen effect and get a lower piezoelectric output voltage (Figure 3.11c).

### 3.3.3 Conclusion

In this part, the CdSe NW array gas sensor was fabricated and measured with/without external power supply. When it is measured at 1.5 V bias, the sensor is able to detect ppm-level NO₂ and NH₃. When it is measured without any power supply, it is still able to detect NO₂ and
NH$_3$. Its self-powered performance comes from the strain-induced ionic polarization in CdSe crystal with wurtzite structure.

### 3.4 Summary

In this chapter, gas sensors based on ZnO/SnO$_2$, ZnO/In$_2$O$_3$, ZnO/WO$_3$ core/shell heterostructures and CdSe NW arrays have been integrated. All these gas sensors can be used to detect oxidizing gas and reducing gas with/without any external power supply. The ZnO/metal oxide core/shell heterostructure NW array gas sensors can detect ppb-level toxic gases at 1.5 V bias, and the CdSe NW array gas sensor can detect ppm-level toxic gases at 1.5 V bias, the different response are mainly due to their different material nature. All these active gas sensors can be operated without power supply and detect high ppm-level gases due to the non-ideal test and work conditions. With an understanding of how different gases affect the sensing and self-powering performance, future studies can focus on optimizing the parameters and perfect the testing and working conditions. Based on these results, the piezopotential created inside ZnO and CdSe NW arrays can be used as self-powered energy source to develop other self-powered systems, such as self-powered photodetector and self-powered multi-functional device.
Reference


ACS Sensors 2016, 1 (10), 1256–1264.


4.1 Introduction

Piezo-phototronic effect, a three way coupling among semiconduction, piezoelectricity, and photon excitation, has attracted much attention since its first application in a ZnO-based UV photodetector, and has widely been applied to enhance the performance of optoelectronic devices, such as solar cells, light emitting diodes, electrochemical processes, and photodetectors, through tuning and controlling charge carrier generation, separation, transport, and/or recombination. As an important II-VI semiconductor, one-dimensional ZnO nanowire has been extensively studied, both theoretically and experimentally, for optoelectronic device applications due to its affordability, abundance in nature, and environmentally friendly fabrication methods. However, ZnO is a wide band gap semiconductor (~3.4 eV), making it incapable of detecting visible light. To overcome this limitation, one strategy is to fabricate a heterojunction structure by forming a staggered type II band alignment where the valence and conduction bands of one semiconductor are lower (or higher) than those of another semiconductor, enabling efficient separation and transportation of photogenerated electrons/holes through spatial confinement. Several type II heterostructures have been applied to improve the performance of the photodetectors, which are capable of
detecting a part of the visible spectrum, however, the detectable maximum wavelength of the reported photodetectors based on type II heterostructures was only able to reach 548 nm (green excitation source). In order to detect the complete visible spectrum, integration of ZnO and ZnSe to form a core/shell type II heterostructure is a promising approach to realize this goal, because of its lower indirect band gap (~1.84 eV).\textsuperscript{22}

In addition, self-powered devices,\textsuperscript{23–27} based on piezoelectric materials, have been demonstrated to effectively power the functional devices, such as photodetectors,\textsuperscript{28,29} gas and humidity sensors,\textsuperscript{30–34} via the harvesting of mechanical energy from the environment, and ultimately, promote electronic device miniaturization and innovation. Among them, self-powered photodetectors, based on the piezo-phototronic effect and powered by the mechanical strain and/or incident light without applying external bias, can significantly boost their optoelectronic performance and environmental adaptability.

In this work, we fabricated a UV/visible photodetector based on type II ZnO/ZnSe heterostructure nanowire array, which was synthesized by a two-step process combining CVD and pulsed laser deposition (PLD) explicated in the previous literature.\textsuperscript{22,35} The details of the ZnO/ZnSe core/shell nanowires growth can be found in the Experimental Section. The ZnO/ZnSe photodetector can detect the whole region of the visible spectrum as well as UV light with external bias; its sensitivity and absolute responsivity was enhanced by one order of magnitude under the application of load and illumination. In addition, the device was also able to operate under no external bias condition behaving as a self-powered photodetector under illumination of UV/visible lights.
4.2 Synthesis of ZnO/ZnSe Core/Shell Nanowire Array

ZnO nanowire array was grown on ZnO coated ITO glass substrate (CG801N, Delta Technologies LTD) through CVD method as mentioned in Chapter 2. Briefly, ITO coated glass substrate was first cleaned by sonicating sequentially in acetone, isopropyl alcohol and deionized water, respectively. Second, 60 nm thick ZnO thin film was sputtered on ITO glass as seed layer, and then 4 gram of Zn powder (99.9%, metals basis, Alfa Aesar) and the ZnO-coated ITO glass substrate were sequentially placed at the first and second zone of the furnace. The first and second zones were heated up to 900 °C and 550 °C under a mixed gas of 300 sccm (standard cubic centimeters per minute) Argon flow and 40 sccm Oxygen flow. The reaction was maintained for 1 hour. The furnace was cooled down naturally to room temperature.

The as-synthesized ZnO nanowire array was then transferred to a home-made PLD system as reported previously.22 A ZnSe target (99.99%, Testbourne Ltd.) and the substrate with as-synthesized ZnO nanowire array were placed in the center of the furnace at a distance of 3 cm, and then a Neodymium-doped Yttrium Aluminum Garnet (Nd:YAG) laser was applied to ablate the ZnSe target for 20 minutes at 500 °C.

4.3 Device Fabrication and Measurement Process

In order to avoid a possible short circuit between top and bottom electrodes, a ~ 2 µm thick PMMA thin layer was first spin-coated on the as-synthesized ZnO/ZnSe core/shell nanowire array. A thin layer of silver (~100 nm) was sputtered on a polyester film with a groove density of 1000 grooves/mm (Edmund Optics) as a top electrode. The top electrode was attached to the top of the ZnO/ZnSe nanowires as shown in Figure 4.1. The unique zigzag morphology (inset in Figure 4.1d) can provide an increased nanowire-electrode contact area and better strain
accommodation. The silver-coated top electrode and ITO bottom electrode were connected to a 2401 source meter (Keithley) through copper leads, respectively. The device was then measured on the platform of a motorized test stand (Mark-10, ESM301L).

4.4 Results and Discussion
4.4.1 Structural Characterization

The structural characterization of ZnO/ZnSe nanowire array is represented in Figure 4.2 where Figure 4.2 a and b are top view low-magnification field emission scanning electron microscope (FESEM) images of the ZnO nanowire array, and ZnO/ZnSe core/shell nanowire array. It can be seen that the ZnO nanowires are perpendicularly grown out with hexagonal tip.

Figure 4.1 Schematic of photodetector fabrication and the measurement process. (a) ZnO nanowire array is grown on ZnO-coated ITO glass via chemical vapor deposition method. (b) ZnSe is coated on ZnO nanowires through pulsed laser ablation. (c) The as-synthesized ZnO/ZnSe nanowire array is integrated using Ag-coated polyester as top electrode. (d) The device and measurement setup. The cross section schematic of the device is shown in the inset.
and the diameters are in the range of 100-120 nm (Figure 4.2a). Figure 4.2b shows that the previously smooth ZnO nanowire surface has been coated by ZnSe, making the surface apparently rough and diameter increase by ~40 nm. In order to confirm the core/shell structure, transmission electron microscopy (TEM) was performed to investigate a single ZnO/ZnSe core/shell nanowire (Figure 4.2c). The sharp interfaces between core (dark) and shell layer (bright) demonstrate a full and uniform coverage of ZnSe on ZnO nanowire surface. Energy dispersive X-ray spectroscopy (EDS) of the single ZnO/ZnSe nanowire (Figure 4.2d) was taken as further evidence to show core/shell nanowire feature. Based on our previous high resolution transmission electron microscopy (HRTEM) observation, the ZnSe shell layer is zinc blende structure.

Figure 4.2 Top view FESEM images of (a) ZnO nanowire array, and (b) ZnO/ZnSe core/shell nanowire array, (c) TEM image of a single ZnO/ZnSe nanowire, and (d) EDS result on the single ZnO/ZnSe nanowire.
4.4.2 Photodetector Measurement under Different Wavelength Excitation Sources

To evaluate the device response, the red (625 nm) excitation source with an intensity of 1.80 × 10^{-3} W/cm² at 1V bias was employed to measure on-off current response of the photodetector, as shown in Figure 4.3a. With the light irradiation on, the current of the photodetector sharply increases from ~287 µA to ~301 µA, and then decreases to ~287 µA when the light is off. The repeatable and stable switching behavior of the photodetector indicates that ZnO/ZnSe core/shell type II structure is very promising for visible light detection.

![Graph](image)

*Figure 4.3 (a) The on-off response of the device under red excitation source at 1V bias. (b) Typical I-V measurement of the photodetector under different excitation sources without load.*

The typical current-voltage measurements of the photodetector were further performed in dark and under illumination of four different wavelength excitation sources, namely, red (625 nm), green (520 nm), blue (465 nm), and UV (385 nm). As seen from Figure 4.3b, the photocurrent significantly rises with an increase in photon energy from 1.98 eV of red (625 nm) with an intensity of 1.80 ×10^{-3}W/cm² to 3.22 eV of UV (385 nm) with an intensity of 1.32 ×10^{-3} W/cm². An increase of 168% in photocurrent (~741 µA) from the device under UV (3.22 eV)
with an intensity of $1.32 \times 10^{-3}$ W/cm$^2$ illumination is attained, compared to the current in dark (~277 µA), which is attributed to the enhanced carrier-separation at the ZnO/ZnSe interface and three transitions resulting from direct band-to-band absorption in ZnO ($E_g \sim 3.2$ eV)$^{35}$ and ZnSe ($E_g \sim 2.7$ eV)$^{36}$ and indirect type II transition between the valence band maxima of ZnSe$_{VBM}$ (shell) and the conduction band minima of ZnO$_{CBM}$ (core)$^{[38-40]}$. It should be noted that the photon energies corresponding to red (1.98 eV), green (2.38 eV) and blue (2.67 eV), are lower than the band gap of ZnO ($E_g \sim 3.2$ eV) and ZnSe ($E_g \sim 2.7$ eV), and are incapable to promote direct band-to-band photoexcitation in either core or shell. Therefore, when the device was irradiated under the red (625 nm), green (520 nm), blue (465 nm) illumination, it is reasonable to believed that the photocurrent response arises from the indirect type II transition of electrons between ZnSe$_{VBM}$ (shell) and the ZnO$_{CBM}$ (core)$^{22,37}$. The peak photocurrents under red (625 nm) with an intensity of $1.80 \times 10^{-3}$ W/cm$^2$, green (520 nm) with an intensity of $3.24 \times 10^{-3}$ W/cm$^2$, and blue (465 nm) with an intensity of $3.0 \times 10^{-3}$ W/cm$^2$ illumination are ~326 µA, ~442 µA and ~536 µA, respectively, which corresponds to an increase of 18% for red (625 nm), 60% for green (520 nm) and 94% for blue (465 nm) excitation sources as compared to the current in dark (~277 µA).

### 4.4.3 Photodetector Measurement under Piezo-Phototronic Effect

It has been well reported that piezopotential generated by strain is able to bend the conduction and valence bands down/up resulting in the increment/decrement in the effective barrier height.$^{12,28,38}$ Figure 4.4a displays a typical $I-V$ measurement of the photodetector under red (625 nm) light illumination and varying compressive loads ranging from 0 N to 2 N, which was applied by a motorized test stand on the device. The full size of the device is 5 mm × 10 mm with a working area of 4 mm × 5 mm. It can be observed that the peak photocurrent significantly
increases proportionally as the compressive load rises, and the peak photocurrent (3.42 mA) at 2 N compressive load is one order of magnitude (~11 times) higher than that (326 µA) at 0 N compressive load. A similar trend of current increment can be observed from I-V measurements under illumination of green (~11 times) (Figure 4.4b) and blue (~10 times) (Figure 4.4c) and UV (10 times) (Figure 4.4d).

Figure 4.4 Typical I-V measurement of the photodetector under varying compressive loads and illumination of (a) red light, (b) green light, (c) blue light and (d) UV light, respectively.
Figure 4.5 (a) The compressive load dependences of photocurrent response, (b) the sensitivity, (c) the responsivity and (d) the percentage change in responsivity of the detector with respect to compressive loads under different wavelength excitation sources from UV to red.

The compressive load dependences of photocurrents \((I_{\text{light}}-I_{\text{dark}})\) at a bias of 1V are plotted in Figure 4.5a. It can be seen that the photocurrent increases with the compressive loads under illumination of red (625 nm), green (520 nm), blue (465 nm) and UV (385 nm) excitation sources. Additionally, the photocurrents \((I_{\text{light}}-I_{\text{dark}})\) at the same compressive load inversely increase with the decrease from the wavelength of the excitation source, which is in agreement with Figure 4.3b. As an important parameter to determine the capability of a photodetector, the sensitivity (Figure 4.5b), defined as \((I_{\text{light}}-I_{\text{dark}})/I_{\text{dark}},^1\) was calculated to be \(1.1\times10^3\%\) for red (625 nm), \(1.6\times10^3\%\) for green (520 nm), \(1.9\times10^3\%\) for blue (465 nm) excitation source and \(2.6\times10^3\%\)
for UV (385 nm) light, which is comparable with other reported type II heterostructure photodetectors based on ZnO/CdS,\textsuperscript{11} ZnO/ZnS,\textsuperscript{35} and CdSe/ZnTe core/shell nanowires.\textsuperscript{39}

Moreover, the performance of the photodetector can also be characterized by its responsivity ($R$),\textsuperscript{11} which is defined as

$$ R = \frac{I_{\text{light}} - I_{\text{dark}}}{P_{\text{ill}}} $$

(4.1)

$$ P_{\text{ill}} = I_{\text{ill}} \times A $$

(4.2)

Where $R$ is the responsivity, $I_{\text{light}}$ is the photocurrent of the photodetector under illumination and $I_{\text{dark}}$ is the current in the dark, $P_{\text{ill}}$ is the illumination power on the photodetector, $I_{\text{ill}}$ is the illumination density and $A$ is the working area of the photodetector. The calculated responsivities (Figure 4.5c) of the photodetector under 2 N compressive load are approximately 8.7 A/W under illumination of red (625 nm) with an intensity of $1.80 \times 10^{-3}$ W/cm$^2$, 6.96 A/W under illumination of green (520 nm) with an intensity of $3.24 \times 10^{-3}$ W/cm$^2$, 8.57 A/W under illumination of blue (465 nm) with an intensity of $3.0 \times 10^{-3}$ W/cm$^2$, and 27.1 A/W under illumination of UV (385 nm) with an intensity of $1.32 \times 10^{-3}$ W/cm$^2$, respectively, which are at least one order of magnitude higher compared to reported broad band photodetector based on type II ZnO/ZnS heterojunction core/shell nanowire array.\textsuperscript{35} The comparative change in responsivity is defined as

$$ \frac{\Delta R}{R_o} \% = \frac{R_{\text{load}} - R_o}{R_0} \times 100\% $$

(4.3)

Where $\Delta R/R_0$ is the comparative change in responsivity,\textsuperscript{10} $R_{\text{load}}$ is the responsivity with compressive load, and $R_0$ is the responsivity without compressive load. The percentage change in
responsivity under 2 N compressive load, as shown in Figure 4.5d, is at least three orders of magnitude higher than that of 0 N compressive load.

4.4.4 Self-Powering Performance of Photodetector

Figure 4.6 The photocurrent response of the device under varying compressive loads at no external bias under (a) red, (b) green, (c) blue and (d) UV excitation source.

Additionally, the photocurrent response of the photodetector with varying compressive loads under red (625 nm) excitation source at no external bias is shown in Figure 4.6a. It can be clearly observed that the photocurrent increases gradually from ~3.4 nA to ~15 nA as the applied compressive load increases from 0 N to 2 N, and a similar phenomenon can be observed when the photodetector was measured under green (520 nm) (Figure 4.6b), blue (465 nm) (Figure 4.6c) and UV (385 nm) (Figure 4.6d) excitation sources.
Figure 4.7 (a) Energy band diagram of a strain-free type-II ZnO/ZnSe heterojunction before the Ag-coated electrode contact is made. The solid lines (green and blue) show the bands of ZnSe and ZnO, and the black dashed line shows Fermi level for both ZnO and ZnSe. (b) Energy band diagram of a strain-free ZnO/ZnSe based photodetector. Ag-coated electrode attached to the top of the ZnSe shell promotes Fermi level realignment that induces band bending. Energy band diagrams of the photodetector (c) under light illumination only and (d) under light illumination and compressive loads, which leads to a piezopotential-induced band bending.

Figure 4.8 Simulated piezo-potential distribution in ZnO core of a single ZnO/ZnSe core/shell nanowire under (a) shear mode (uniaxial compression combined with bending), (b) uniaxial compression mode, and (c) bending mode.
The vertical color gradient represents the distribution of piezo-potential in the interior of ZnO nanowire. This simulation neglects any piezo-potential contribution from the zinc-blend ZnSe shell.

The mechanism of the strain-induced photoresponse of the photodetector is explained by piezo-phototronic effect, which is shown in Figure 4.7. Figure 4.7a shows an abrupt type II energy band alignment of ZnO/ZnSe heterojunction before the Ag-coated top electrode contacts with the nanowires.\textsuperscript{[23]} Once the Ag-coated top electrode contacts with the nanowires, the net free electrons transfer from Ag to the shell of ZnSe and ZnO to realign the Fermi level of ZnSe and ZnO, resulting in slight downward bending of ZnSe and ZnO conduction and valence bands, as shown in Figure 4.7b. $\Delta \Phi_1$ and $\Delta \Phi_2$ represent the hole and electron trap state barriers which are unfavorable for charge transport and can be tuned by the piezopotential induced in the interior of ZnO nanowire. When the photodetector is illuminated by excitation sources with different wavelengths, the electron-hole pairs are generated from indirect type II transition between the ZnSe\textsubscript{VBM} (shell) and ZnO\textsubscript{CBM} (core) ($E_g \sim 1.84$ eV) and/or direct band-to-band absorption in ZnO ($E_g \sim 3.2$ eV) and ZnSe ($E_g \sim 2.7$ eV), as shown in Figure 4.7c. Upon compression of the photodetector, there exists the possibility of three elastic deformation modes,\textsuperscript{35} as shown in Figure 4.8, for ZnO nanowires: shear mode, uniaxial compression mode, and bending mode. In consideration of the ZnO nanowire growth on a slightly off-axis oriented and high length ($\sim 5\mu$m)/diameter ($\sim 150$ nm) aspect ratio, it is believed that most of the ZnO nanowires undergo shear or compression deformation as shown in Figure 4.8 a and b, which generated localized negative polarization charges on the top of ZnO nanowires, although a few of nanowires could be under bending mode (Figure 4.8 c). The shear or compression strain-induced localized negative polarization charges in ZnO at the interface between ZnO and ZnSe is able to bend the edges of valence and conduction bands of ZnO upward to a higher energy state as shown in Figure 4.7d,\textsuperscript{3,40} which reduces the effective barrier height between ZnO and ZnSe,
thus resulting in an increment of the peak photocurrent with external bias, as shown in Figure 4.4. Additionally, the increment of the peak current at no external bias condition, shown in Figure 4.6, gives the device self-powered photodetection capability.

4.5 Conclusion

In summary, a broad band photodetector (UV/visible) has been successfully integrated using type II ZnO/ZnSe core/shell heterostructure nanowire array. The photodetector exhibited strong and stable response to UV excitation source as well as the whole visible spectrum, particularly from red excitation source to blue excitation source. The absolute sensitivity and the percentage change in responsivity of the photodetector were enhanced by one and three orders of magnitude, respectively, owing to the unique type II heterostructure and the piezo-phototronic effect under applied compressive load. Furthermore, the device displays self-powered photodetection behavior under UV and whole visible light illumination, which demonstrates a promising application of ZnO/ZnSe type II core/shell nanowire array in powered and self-powered UV/Visible photodetection.


(13) Soci, C.; Zhang, A.; Xiang, B.; Dayeh, S. A.; Aplin, D. P. R.; Park, J.; Bao, X. Y.; Lo, Y.


(27) Ding, J.; Fang, H.; Lian, Z.; Li, J.; Lv, Q.; Wang, L.; Sun, J.-L.; Yan, Q. A Self-Powered
Photodetector Based on a CH3NH3PbI3 Single Crystal with Asymmetric Electrodes. CrystEngComm 2016, 18 (23), 4405–4411.


Chapter 5 Piezo-Magnetotronic and Piezo-Photo-Magnetotronic Effects in ZnO and ZnO/Co$_3$O$_4$ Nanowire Arrays

5.1 Introduction

Recently, multi-property coupling effects based on piezoelectric semiconductors have generated a profound impact on exploring innovative electronic device applications in transistors$^{1-4}$, sensors$^{5-9}$ and energy harvesting devices.$^{10-16}$ Piezotronic effect is a typical two-way coupling effect between piezoelectricity and semiconductor properties in materials with asymmetric crystal structure and can be used to convert mechanical energy into electrical energy or develop novel electronic devices with much enhanced performance through controlling the transport behavior of charge carriers.$^{17}$ Based on this phenomenon, piezo-phototronics has been further proposed by coupling piezotronic effect with photoexcitation to enhance the performance of optoelectronic devices by modulating the generation, separation, recombination and transport of photo-induced electron-hole pairs.$^{18}$ These are the fundamental principle of piezotronics and piezo-phototronics. On the other hand, it is well-known that magnetic field is widely implemented in numerous areas,$^{19}$ such as data storage,$^{20-22}$ medical diagnostics,$^{23}$ electromagnetic sensing,$^{24}$ etc. The various applications of magnetic fields are mainly based on electromagnetic induction, Hall Effect, magnetostriction, etc. Very recently, several studies on coupling magnetic fields to piezotronics/piezo-phototronic effects have been reported.$^{1,24-26}$ For instance, Wang group proposed a magnetic-induced-piezopotential field-effect transistor on multilayer structure by coupling magnetic field with the piezotronic effect (piezo-magnetotronic effect),$^1$ in which the piezopotential inside piezoelectric material was triggered by the deformation of the magnetic layer when magnetic field was applied, and was used to modulate the carrier transport of the channel layer. A magnetic-induced-luminescence multilayer device
was also reported by Hao group through coupling the magnetic field with the piezo-phototronic effect (piezo-photo-magnetotronic effect).\textsuperscript{27} The strain generated by the magnetic elastomer resulted in a piezopotential inside the piezoelectric phosphor composite, which was applied to control the light emission. It should be noted, however, that the magnetic field in the above mentioned magnetic-related coupling effects is applied on magnetic layer based on magnetostriction, and to our best knowledge, there is no report on piezo-magnetotronic and piezo-photo-magnetotronic effects where the magnetic field is directly applied on piezoelectric semiconductors to control the charge carrier flow.

In this work, ZnO nanowire (NW) array, as one of most commonly used piezoelectric materials in the emerging fields of piezotronics and piezo-phototronics,\textsuperscript{17,28,29} is chosen to investigate the coupling effects of piezoelectricity, magnetic field and photoexcitation. Electron flow inside ZnO NW will be affected by Lorentz Force when a magnetic field is engaged perpendicularly to the NW. By applying an external stress on ZnO NW array, the magnetic-induced current responses are much magnified due to piezo-magnetotronic effect. Under UV light illumination, the current becomes larger when the magnetic field is engaged since magnetic field is favorable to the separation of photo-induced electron-hole pairs. Moreover, the magnetic-induced current response under UV light illumination is further improved by piezo-photo-magnetotronic effect. In addition, a ZnO/Co3O4 core/shell heterostructure has also been investigated and offers a further improvement of the current response in comparison to ZnO under the same condition.
5.2 Experiment

5.2.1 Synthesis of ZnO Nanowire Array

ZnO NW array was first synthesized on SiO$_2$ passivated indium tin oxide (ITO) coated glass substrate (CG801N, Delta Technologies LTD) through chemical vapor deposition in a three-zone tube furnace (GSL-1400X, MTI Corp.). In brief, the substrate was first cleaned by sonicating sequentially in acetone, isopropyl alcohol and deionized water, respectively. Second, Zn powders (99.9%, metals basis, Alfa Aesar) and the cleaned substrate were sequentially placed at the center zone and the right zone of the furnace. The center zone and the right zone were heated up to 900 °C and 550 °C at a rate of 10 °C/min, respectively, under a mixed gas of 300 sccm (standard cubic centimeters per minute) Argon flow and 40 sccm Oxygen flow. The reaction was maintained for 1 hour. The furnace was then cooled down naturally to room temperature.

5.2.2 Synthesis of ZnO/Co$_3$O$_4$ Core/Shell Nanowire Array

10 mM of cobalt (II) nitrate hexahydrate (Co(NO$_3$)$_2$•6H$_2$O) (98%, reagent grade, Sigma-Aldrich) and hexamine (HMT) solution were dissolved into 40 mL of deionized water with molar concentrations and stirred for 1 hour at room temperature. The as-synthesized ZnO NW array was cut into two pieces. One piece of ZnO NW array was used as control sample, and another one was put in the nutrition solution, and the solution was heated and maintained at 95 °C for 12 hours as reported previously. After synthesis, the substrate was washed with deionized water and then annealed at 450 °C for 2 hours.
5.2.3 Material Characterizations

![Figure 5.1](image)

Figure 5.1 FESEM images of (a) pristine ZnO NWs and (b) ZnO/Co$_3$O$_4$ core/shell NWs, insets in a and b are the high-resolution images. (c) TEM image of a single ZnO/Co$_3$O$_4$ core/shell NW with corresponding (d) SAED pattern and (e) EDS spectrum. (f) XRD pattern of pristine ZnO NWs and ZnO/Co$_3$O$_4$ core/shell NWs.

The structural characterization of ZnO and ZnO/Co$_3$O$_4$ NW arrays is represented in Figure 5.1. It can be seen from the field emission scanning electron microscope (FESEM) image in Figure 5.1a that the ZnO NWs are randomly grown out with smooth surface and the inset in Figure 5.1a reveals the hexagonal structure of ZnO NWs with diameter in the range of 150-200 nm. The FESEM image in Figure 5.1b shows that the ZnO/Co$_3$O$_4$ NWs remain similar in size and density with pristine ZnO NWs and it can be observed from the enlarged FESEM image (inset in Figure 5.1 b) that the previously smooth surface of the pristine ZnO NWs becomes rough. The TEM image of a single ZnO/Co$_3$O$_4$ NW in Figure 5.1c demonstrates that the ZnO
NW is fully covered by the Co$_3$O$_4$ shell with the thickness of ~10 nm. The corresponding SAED pattern in Figure 5.1d reveals the diffraction pattern of ZnO core and continuous well-defined diffraction rings of Co$_3$O$_4$ shell, indicating single crystalline nature of ZnO core and polycrystalline nature of Co$_3$O$_4$ shell. The diffraction pattern of ZnO core confirms that it is well crystallized with wurtzite structure and grown along c-axis direction. The diffraction rings of Co$_3$O$_4$ shell can be indexed to (111), (220), (311), (400), (511), and (440) lattice planes of the cubic structure (space group Fd3m), which is well consistent with the XRD result discussed below.

In order to further confirm the element composition of ZnO/Co$_3$O$_4$ NWs, Energy dispersive spectroscopy (EDS) spectrum of a single ZnO/Co$_3$O$_4$ NW was displayed in Figure 5.1e, which reveals the existence of cobalt, zinc and oxygen, and the EDS peaks of carbon and copper come from TEM sample holder and grid. To investigate the crystallinity and crystal phase of the pristine ZnO NWs and ZnO/Co$_3$O$_4$ NWs, their X-ray diffraction (XRD) spectra were recorded in Figure 5.1f. The XRD spectrum of the pristine ZnO NWs exhibits a typical XRD pattern of the ZnO NWs with high-purity wurtzite hexagonal phase, where a strong and sharp diffraction peak and several relative weak peaks appear at around 34.4°, 47.5°, 56.6°, 62.8° and 69.1°, respectively, representing (002), (102), (110), (103) and (201) planes of the hexagonal structure, matching well with standard hexagonal ZnO (JCPDS CARD No. 36-1451). This XRD pattern confirms that the ZnO NWs grow along the c-axis and is in agreement with its diffraction pattern in Figure 5.1d. The XRD spectrum of ZnO/Co$_3$O$_4$ NWs in Figure 5.1f indicates a very similar pattern with the pristine ZnO NWs except some weak diffraction peaks at around 19.0°, 31.3°, 36.8°, 44.8° and 65.2° which are well corresponding to the cubic phase of the Co$_3$O$_4$ (JCPDS card No. 073-1701), representing (111), (220), (311), (400) and (440) planes,
respectively.\textsuperscript{30} This XRD result is also in well agreement with the diffraction rings of Co\textsubscript{3}O\textsubscript{4} shell in Figure 5.1d and confirms the formation of cobalt oxide phase.

\subsection*{5.2.4 Device Fabrication and Measurement Process}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{device fabrication process}
\caption{Schematic illustration of the device fabrication and the measurement process. (a) as-synthesized ZnO or ZnO/Co\textsubscript{3}O\textsubscript{4} NWs on ITO glass substrate, (b) a \textasciitilde{}2 \textmu{}m PMMA layer was spin-coated onto the NWs, (c) the device was integrated with Ag-coated top electrode and (d) the device was located on homemade stage where load was applied on top of the device, UV light was illuminated from the bottom of the device and magnetic field was applied perpendicularly to the NWs.}
\end{figure}

In order to support NWs and avoid a possible short circuit between top and bottom electrodes, a \textasciitilde{}2 \textmu{}m thick layer of PMMA was first spin-coated on ZnO or ZnO/Co\textsubscript{3}O\textsubscript{4} NWs. A 100 nm thick Ag thin film was then sputtered on a polyester film as a top electrode, which has a unique zigzag morphology and offers an additional NWs-electrode contact area and better strain.
accommodation. The top electrode was attached to the top of the ZnO or ZnO/Co$_3$O$_4$ NWs as shown in Figure 5.2. The silver-coated top electrode and ITO bottom electrode were connected to a 2401 source meter (Keithley) through copper leads. The magnetic field was applied perpendicularly to NWs, and the force was applied on top of the device on the platform of a motorized test stand (Mark-10, ESM301L).

5.3 Results and Discussion

5.3.1 Piezo-Magnetotronic Effect

Before evaluating the coupling effect between magnetic field and piezotronic effect, the ZnO NW array was first tested under magnetic field. The current-voltage (I-V) characteristics are illustrated in Figure 5.3a. The rectifying property of the I-V curves indicated that a Schottky barrier was formed between ZnO NWs and Ag electrode. It can be observed that the peak currents of ZnO decreased from 3.0 µA to 2.1 µA as the external magnetic field increased from 0 to 180 Gauss (G). A part of the free electrons inside ZnO NWs were forced to move toward the surface of ZnO NWs due to Lorentz Force, hereby forcing a part of free electrons to gravitate toward the surface of ZnO NWs due to Lorentz Force caused by the magnetic field. According to oxygen-related electron-trap filling mechanism, the electrons were trapped by the surface defects or adsorbed by oxygen ions in air as presented in region I of Figure 5.3f, therefore, the number of free electrons was reduced, resulting in an increment of the resistance of ZnO NW. Besides, the electron accumulation at the ZnO NW surface generated a depletion region near the surface of ZnO NWs, which further increased the resistance of ZnO NWs. It should be noted that the peak current of ZnO is inversely proportional to the magnetic field strength, because the number of the trapped/accumulated electrons at the surface of ZnO NW become larger as the magnetic field strength increased, resulting in a decrement of the conductivity of NW. In order to
investigate the coupling effect between piezotronic effect and magnetic field, the ZnO NW array was measured with stresses from 0.5 N to 1.5 N as indicated in Figure 5.3 b, c and d. It can be observed that the peak current significantly increased with an increment of the stress due to piezotronic effect. According to a previous report, potential barrier height modulation generally makes more significant contribution to current response than depletion layer modulation, therefore, we believe that the enhancement of the peak currents is mainly due to the strain-induced piezopotential inside ZnO NWs (region II of Figure 5.3f). When the force was applied to the NW, the NW was bent due to its randomly growing direction and then the strain-induced positive piezopotential was generated at the surface of ZnO NW which lowered the Schottky Barrier Height (SBH) between ZnO and Ag, resulting in a significant increment of the peak current. The magnitude of the piezopotential is dependent on the degree of mechanical deformation, thus highest peak current is gained at 1.5 N stress, and the peak currents with 1.5 N stress in both the absence and presence of magnetic field are at least one order of magnitude higher than that with 0 N stress. The piezotronic effect enhanced peak currents also decreased by applying a magnetic field. The magnetic-induced peak current differences \( \Delta I = I_B - I_0 \), where \( I_B \) and \( I_0 \) are the peak currents with and without magnetic field, respectively) of ZnO NWs with different magnetic field strength and stresses are summarized in Figure 5.3e, and it can be observed that the peak current differences are magnified as the magnetic field strength and stress increased. The absolute peak current difference (10.1 µA) with 1.5 N stress is 10 times larger than that (0.9 µA) with 0 N stress, which demonstrates that the piezo-magnetotronic effect can enlarge the magnetic-induced current response.
To further demonstrate the piezo-magnetotronic coupling effect and improve the magnetic-induced current response, we designed further experiments by fabrication of the ZnO/Co$_3$O$_4$ core/shell NW array. Figure 5.4a illustrates the $I$-$V$ curves of ZnO/Co$_3$O$_4$ NW array in absence of stress under magnetic field. Compared to the $I$-$V$ curves of ZnO device in Figure 5.3a, it can be observed that the magnetic-induced peak currents of ZnO/Co$_3$O$_4$ decreased from 9.9 $\mu$A to 4.8 $\mu$A as the magnetic field increased from 0 to 180 G. The absolute peak current difference (5.1 $\mu$A) is 5 times larger than that (0.9 $\mu$A) of ZnO because of the precipitation of Co$_3$O$_4$ and its rough surface, which created crystallographic defects at the ZnO/Co$_3$O$_4$ interface due to the lattice mismatch between the two materials, and provided preferential adsorption site for oxygen molecules (region I of Figure 5.4f), compared to the smooth surface of ZnO NWs. The ZnO/Co$_3$O$_4$ NW array was then measured with different stresses from 0.5 N to 1.5 N exhibited in (Figure 5.4b, c and d). Corresponding to potential barrier height modulation, when
the force was applied to the core/shell NWs, the core ZnO NWs were bent and the strain-induced positive piezopotential lowered the SBHs of ZnO/Co$_3$O$_4$ and Co$_3$O$_4$/Ag (region II of Figure 5.4f) which resulted in a large increment of the peak current of ZnO/Co$_3$O$_4$ NW array. When it’s measured under magnetic field, more electrons were forced by the magnetic field to move towards the surface resulting in a large decrement of peak currents. All the peak current differences of ZnO/Co$_3$O$_4$ NW array are summarized in Figure 5.4e, and it can be seen that the absolute peak current difference (91.8 µA) of ZnO/Co$_3$O$_4$ NW are 9 times larger than that (10.1 µA) of ZnO NW array under the same conditions due to the significant increment of current the core/shell structure, which proves the core/shell heterostructure is capable of enhancement of the magnetic-induced current response.

Figure 5.4 I-V characteristics of ZnO/Co$_3$O$_4$ NWs device under (a) 0 N (b) 0.5, (c) 1 and (d) 1.5 N stress. (e) The summary of the peak current difference of the device under various stresses. (f) Schematics of energy bands alignment and electron movement under magnetic field which is directed perpendicularly out of the screen.
5.3.2 Piezo-Photo-Magnetotronic Effect

Figure 5.5 I-V characteristics of ZnO NWs device under UV illumination and (a) 0 N (b) 0.5, (c) 1 and (d) 1.5 N stress. (e) The summary of the peak current difference of the device under various stresses. (f) Schematics of energy bands alignment and electron movement under magnetic field which is directed perpendicularly out of the screen.

In order to investigate the coupling effect between magnetic field and piezo-phototronic effect, the ZnO NW array was measured under magnetic field and UV light illumination (Figure 5.5a). The peak current (102 µA) under UV light illumination is 35 times higher than that (3 µA) without UV light illumination because a massive number of photo-induced electron-hole pairs were generated inside ZnO NWs and a part of photo-induced holes migrated to the surface of ZnO NWs and detached the adsorbed oxygen ions from the ZnO surface, and therefore the unpaired and released electrons further increased the conductivity of ZnO NWs with a decrement of the width of depletion layer as shown in region I of Figure 5.5f. Surprisingly, the peak current of ZnO NW array increased from 102 µA to 132 µA under UV illumination as magnetic field increased from 0 to 180 G. This opposite magnetic-induced peak current trend might be mainly
due to the following two effects: a part of electrons migrated to the surface of NW due to Lorentz Force when the current flowed along the NWs, which has a negative effect on the conductivity of NW. On the other hand, magnetic field is favorable to the separation of photo-induced electron-hole pairs and unfavorable to the recombination of electron-hole pairs, which prolongs electron lifetime and has a positive effect on the conductivity of NW. This positive effect makes a much larger contribution than the negative effect to the current response of the device\textsuperscript{34} (region II of Figure 5.5f), resulting in an increment of the peak current as the magnetic field increase. The ZnO NW array was also measured under different stress of 0.5, 1, and 1.5 N and the typical I-V curves are shown in Figure 5.5 b, c and d. It can be seen that the peak current increased when a stress was applied because the strain-induced positive piezopotential decreased the SBH between ZnO and Ag (region III of Figure 5.5f). The peak current also increased as the magnetic field increased. All peak current difference results are summarized in Figure 5.5e. The peak current difference is proportional to the magnetic field strength with/without stress and the absolute largest peak current difference (146 µA) of ZnO NWs is magnified at least two orders of magnitude by piezo-photo-magnetotronic effect compared to the peak current difference (0.9 µA) of ZnO NWs under magnetic field, which demonstrates the piezo-photo-magnetotronic effect can further enhance the magnetic-induced current response.
Figure 5.6 I-V characteristics of ZnO/Co$_3$O$_4$ NWs device under UV illumination and (a) 0 N (b) 0.5, (c) 1 and (d) 1.5 N stress. (e) The summary of the peak current difference of the device under various stresses. (f) Schematics of energy bands alignment and electron movement under magnetic field which is directed perpendicularly out of the screen.

On the other side, the coupling effect between magnetic field and piezo-phototronic effect was also investigated on ZnO/Co$_3$O$_4$ NW array. The ZnO/Co$_3$O$_4$ NW array was measured under UV light illumination with 0, 0.5, 1 and 1 N and the I-V curves are shown in Figure 5.6a, b, c and d, respectively. The peak current of ZnO/Co$_3$O$_4$ NW array under UV illumination is much larger than that of ZnO NW array under UV illumination due to small band gap of Co$_3$O$_4$ (~2.3 eV) and core/shell heterojunction. When it’s measured under UV light illumination, photo-induced electron-hole pairs were generated inside ZnO NWs, Co$_3$O$_4$ NWs and at the interface between ZnO and Co$_3$O$_4$ (region I of Figure 5.6f), resulting in a large increment of the current. Moreover, the core/shell heterostructure is beneficial to the separation of electrons and holes into different spatial regions, further increasing the amount of free electrons. These synergistic effects resulted in a significant increment of the amount of free electrons and the peak current of the
ZnO/Co\textsubscript{3}O\textsubscript{4}NW array. When it’s measured under magnetic field, more electrons were affected by Lorentz Force (region II of Figure 5.6f), resulting in a larger magnetic-induced peak current difference in comparison to ZnO. When stress was applied on NWs, the peak current increased significantly since the strain-induced positive piezopotential inside ZnO NWs lowered the SBHs of ZnO/Co\textsubscript{3}O\textsubscript{4} and Co\textsubscript{3}O\textsubscript{4}/Ag shown (region III of Figure 5.6f), which resulted in additional electrons movement to the surface of ZnO NWs, and therefore gave rise to a larger peak current difference. Figure 5.6e summarized all the peak current differences of ZnO/Co\textsubscript{3}O\textsubscript{4} NW array which demonstrates that the peak current difference increases as the stress and magnetic field strength increases, and the increment is proportional to the stress and magnetic field strength. The largest peak current (471 µA) of ZnO/Co\textsubscript{3}O\textsubscript{4} NWs based on piezo-photo-magnetotronic effect is gained at 1.5 N and 180 G, which is 3 times larger than the peak current (146 µA) of ZnO NWs device under the same condition.

5.4 Conclusion

In summary, ZnO NWs and ZnO/Co\textsubscript{3}O\textsubscript{4} core/shell NW arrays have been used to explore the piezo-magnetotronic and piezo-photo-magnetotronic coupling effects. As magnetic field was applied, the current response decreased, and the peak current difference was magnified by at least one order of magnitude through employing a stress due to piezo-magnetotronic effect. Under UV light illumination, the current response increased with increase of magnetic field strength because magnetic field is favorable to the separation of photo-induced electron-hole pairs. Their absolute magnetic-induced peak current differences are boosted by two orders due to piezo-photo-magnetotronic effect. In addition, a further improvement of the magnetic-induced current responses based on ZnO/Co\textsubscript{3}O\textsubscript{4} core/shell heterojunction was achieved because the core/shell structure is favorable to the separation of photo-induced electron-hole pairs resulting
in a large increment of the peak current. The results in this work demonstrate potential applications in next generation of self-powered multi-functional devices based on piezo-magnetotronic and piezo-photo-magnetotronic effects.
Reference


Chapter 6 Concluding Remarks

The main goal of this work was to investigate the multi-property coupling effects among piezoelectricity, photoexcitation, magnetic field and semiconductor properties based on three dimensional II-VI semiconductor nanowire arrays and to develop self-powered multi-functional sensors based on the piezotronic, piezo-phototronic, piezo-magnetotronic and piezo-photo-magnetotronic effects. Herein, ZnO and CdSe nanowire arrays have been chosen as the piezoelectric materials to power the sensors.

Through coupling the piezotronic and gas sensing properties of II-VI semiconductors, self-powered gas sensors based on ZnO/SnO$_2$, ZnO/In$_2$O$_3$, ZnO/WO$_3$ core/shell heterostructures and CdSe NW arrays have been proposed in Chapter 3. ZnO and CdSe nanowire arrays can convert mechanical energy into electricity to power the sensors as well as detect the target gases. These active gas sensors can detect oxidizing gas and reducing gas at ppm or ppb level with/without any power supply. This innovative type of conceptual design opens a new direction for the development of the next generation of self-powered sensors and expands the scope of self-powered nanosystems.

A ZnO/ZnSe heterostructure core/shell nanowire array UV/visible photodetector based on piezo-phototronic effect has been demonstrated in Chapter 4. Piezo-phototronic effect is a three-way coupling effect among piezoelectricity, photoexcitation and semiconductor properties, which is able to be used to enhance the performance of optoelectronic devices by modulating the generation, separation, recombination and transport of photo-induced electron-hole pairs. This photodetector can detect the entire range of the visible spectrum as well as UV light, and its performance is largely enhanced by piezo-phototronic effect. Furthermore, the photodetector can detect UV and visible light without any power supply. This experiment offers an approach to
expand the photo detection range by using type II heterostructure core/shell nanowire array in both powered and self-powered conditions.

The multi-field coupling effects among magnetic field, piezoelectricity and photoexcitation have been investigated in ZnO and ZnO/Co$_3$O$_4$ nanowire arrays in Chapter 5. The magnetic-induced current response of ZnO nanowire array declined with decrement of magnetic field, and was magnified by one order of magnitude through applying an external stress due to piezo-magnetotronic effect. In contrast, the current response under UV light illumination increased as magnetic field increased. The current response is further enhanced by at least two orders due to piezo-photo-magnetotronic effect. Furthermore, ZnO/Co$_3$O$_4$ core/shell heterojunction was employed to improve the current responses up to 9 times and 3 times, under piezo-magnetotronic and piezo-photo-magnetotronic engagements, respectively, attributed to the improved charge carrier separation and transportation at the core/shell interface. This study not only explores the concept of piezo-magnetotronic and piezo-photo-magnetotronic effects, but also demonstrates great potential of piezoelectric-related multi-property coupling effects in applications of multi-functional devices.

In summary, this dissertation studied the piezoelectric-related multi-property coupling effects on semiconductor materials and explored potential applications based on these coupling effects. The piezoelectric-related multi-property coupling effects have been investigated in three dimensional II-VI semiconductor nanowire arrays. The applications as self-powered/multi-functional sensors, such as self-powered gas sensor, self-powered photodetector and multi-functional sensors, have also been demonstrated. The design concept of self-powered system and multi-functional devices based on piezoelectric-related coupling effects is quite significant in developing next generation of multi-functional sensors with self-powered properties.
Appendix: Copyright Permissions

<table>
<thead>
<tr>
<th>License Number</th>
<th>4334840376002</th>
</tr>
</thead>
<tbody>
<tr>
<td>License date</td>
<td>Apr 23, 2018</td>
</tr>
<tr>
<td>Licensed content publisher</td>
<td>Oxford University Press</td>
</tr>
<tr>
<td>Licensed content publication</td>
<td>National Science Review</td>
</tr>
<tr>
<td>Licensed content title</td>
<td>Piezotronics and piezo-phototronics: fundamentals and applications</td>
</tr>
<tr>
<td>Licensed content author</td>
<td>Wang, Zhong Lin; Wu, Wenzhuo</td>
</tr>
<tr>
<td>Licensed content date</td>
<td>Dec 12, 2013</td>
</tr>
<tr>
<td>Type of Use</td>
<td>Thesis/Dissertation</td>
</tr>
<tr>
<td>Institution name</td>
<td></td>
</tr>
<tr>
<td>Title of your work</td>
<td>II-VI Semiconductor Nanowire Array Sensors Based on Piezotronic, Piezo-Phototronic and Piezo-Photo-Magnetotronic Effects</td>
</tr>
<tr>
<td>Publisher of your work</td>
<td>University of New Orleans</td>
</tr>
<tr>
<td>Expected publication date</td>
<td>Apr 2018</td>
</tr>
<tr>
<td>Permissions cost</td>
<td>0.00 USD</td>
</tr>
<tr>
<td>Value added tax</td>
<td>0.00 USD</td>
</tr>
<tr>
<td>Total</td>
<td>0.00 USD</td>
</tr>
<tr>
<td>Title</td>
<td>II-VI Semiconductor Nanowire Array Sensors Based on Piezotronic, Piezo-Phototronic and Piezo-Photo-Magnetotronic Effects</td>
</tr>
<tr>
<td>Instructor name</td>
<td>Shuke Yan</td>
</tr>
<tr>
<td>Institution name</td>
<td>University of New Orleans</td>
</tr>
<tr>
<td>Expected presentation date</td>
<td>Apr 2018</td>
</tr>
<tr>
<td>Order reference number</td>
<td>15</td>
</tr>
<tr>
<td>Portions</td>
<td>Figures 2, 4,5,6 and 9</td>
</tr>
<tr>
<td>Requestor Location</td>
<td>Shuke Yan</td>
</tr>
<tr>
<td></td>
<td>2000 Lakeshore Dr.</td>
</tr>
<tr>
<td></td>
<td>NEW ORLEANS, LA 70148 United States</td>
</tr>
<tr>
<td></td>
<td>Attn: Shuke Yan</td>
</tr>
<tr>
<td>Publisher Tax ID</td>
<td>GB125506730</td>
</tr>
<tr>
<td>Billing Type</td>
<td>Invoice</td>
</tr>
<tr>
<td>Billing Address</td>
<td>Shuke Yan</td>
</tr>
<tr>
<td></td>
<td>2000 Lakeshore Dr.</td>
</tr>
</tbody>
</table>
STANDARD TERMS AND CONDITIONS FOR REPRODUCTION OF MATERIAL
FROM AN OXFORD UNIVERSITY PRESS JOURNAL

1. Use of the material is restricted to the type of use specified in your order details.
2. This permission covers the use of the material in the English language in the following territory:
world. If you have requested additional permission to translate this material, the terms and
conditions of this reuse will be set out in clause 12.
3. This permission is limited to the particular use authorized in (1) above and does not allow you to
sanction its use elsewhere in any other format other than specified above, nor does it apply to
quotations, images, artistic works etc that have been reproduced from other sources which may be
part of the material to be used.
4. No alteration, omission or addition is made to the material without our written consent.
Permission must be re-cleared with Oxford University Press if you decide to reprint.
5. The following credit line appears wherever the material is used: author, title, journal, year,
volume, issue number, pagination, by permission of Oxford University Press or the sponsoring
society if the journal is a society journal. Where a journal is being published on behalf of a learned
society, the details of that society must be included in the credit line.
6. For the reproduction of a full article from an Oxford University Press journal for whatever
purpose, the corresponding author of the material concerned should be informed of the proposed
use. Contact details for the corresponding authors of all Oxford University Press journal contact
can be found alongside each abstract or full text of the article concerned, accessible from
www.oxfordjournals.org. Should there be a problem clearing these rights, please contact
journals.permissions@oup.com.
7. If the credit line or acknowledgement in our publication indicates that any of the figures, images
or photos was reproduced, drawn or modified from an earlier source it will be necessary for you to
clear this permission with the original publisher as well. If this permission has not been obtained,
please note that this material cannot be included in your publication/photocopies.
8. While you may exercise the rights licensed immediately upon issuance of the license at the end of
the licensing process for the transaction, provided that you have disclosed complete and accurate
details of your proposed use, no license is finally effective unless and until full payment is received
from you (either by Oxford University Press or by Copyright Clearance Center (CCC)) as
provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a
timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall
be void as if never granted. Further, in the event that you breach any of these terms and conditions
or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and
shall be void as if never granted. Use of materials as described in a revoked license, as well as any
use of the materials beyond the scope of an unrevoked license, may constitute copyright
infringement and Oxford University Press reserves the right to take any and all action to protect its
copyright in the materials.
9. This license is personal to you and may not be sublicensed, assigned or transferred by you to any
other person without Oxford University Press’s written permission.
10. Oxford University Press reserves all rights not specifically granted in the combination of (i) the
license details provided by you and accepted in the course of this licensing transaction, (ii) these
terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

https://is1000.copyright.com/AppDispatchServlet
<table>
<thead>
<tr>
<th>License Number</th>
<th>4334841378965</th>
</tr>
</thead>
<tbody>
<tr>
<td>License date</td>
<td>Apr 23, 2018</td>
</tr>
<tr>
<td>Licensed Content Publisher</td>
<td>Elsevier</td>
</tr>
<tr>
<td>Licensed Content Publication</td>
<td>Nano Today</td>
</tr>
<tr>
<td>Licensed Content Title</td>
<td>Piezopotential gated nanowire devices: Piezotronics and piezo-phototronics</td>
</tr>
<tr>
<td>Licensed Content Author</td>
<td>Zhong Lin Wang</td>
</tr>
<tr>
<td>Licensed Content Date</td>
<td>Dec 1, 2010</td>
</tr>
<tr>
<td>Licensed Content Volume</td>
<td>5</td>
</tr>
<tr>
<td>Licensed Content Issue</td>
<td>6</td>
</tr>
<tr>
<td>Licensed Content Pages</td>
<td>13</td>
</tr>
<tr>
<td>Start Page</td>
<td>540</td>
</tr>
<tr>
<td>End Page</td>
<td>552</td>
</tr>
<tr>
<td>Type of Use</td>
<td>reuse in a thesis/dissertation</td>
</tr>
<tr>
<td>Intended publisher of new work</td>
<td>other</td>
</tr>
<tr>
<td>Portion</td>
<td>figures/tables/illustrations</td>
</tr>
<tr>
<td>Number of figures/tables/illustrations</td>
<td>1</td>
</tr>
<tr>
<td>Format</td>
<td>electronic</td>
</tr>
<tr>
<td>Are you the author of this Elsevier article?</td>
<td>No</td>
</tr>
<tr>
<td>Will you be translating?</td>
<td>No</td>
</tr>
<tr>
<td>Order reference number</td>
<td>17</td>
</tr>
<tr>
<td>Original figure numbers</td>
<td>Figure 5</td>
</tr>
<tr>
<td>Title of your thesis/dissertation</td>
<td>II-VI Semiconductor Nanowire Array Sensors Based on Piezotronic, Piezo-Phototronic and Piezo-Photo-Magnetotronic Effects</td>
</tr>
<tr>
<td>Publisher of new work</td>
<td>University of New Orleans</td>
</tr>
<tr>
<td>Author of new work</td>
<td>Shuke Yan</td>
</tr>
<tr>
<td>Expected completion date</td>
<td>Apr 2018</td>
</tr>
<tr>
<td>Estimated size (number of pages)</td>
<td>1</td>
</tr>
<tr>
<td>Requestor Location</td>
<td>Shuke Yan</td>
</tr>
</tbody>
</table>

2000 Lakeshore Dr.

NEW ORLEANS, LA 70148
United States
Attn: Shuke Yan
INTRODUCTION
1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com.

GENERAL TERMS
2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows: "Reprinted from Publication title, Vol. edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC’s Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC’s Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out
This Agreement between Shuke Yan ("You") and Springer Nature ("Springer Nature") consists of your license details and the terms and conditions provided by Springer Nature and Copyright Clearance Center.

<table>
<thead>
<tr>
<th>License Number</th>
<th>4335031006304</th>
</tr>
</thead>
<tbody>
<tr>
<td>License date</td>
<td>Apr 23, 2018</td>
</tr>
<tr>
<td>Licensed Content Publisher</td>
<td>Springer Nature</td>
</tr>
<tr>
<td>Licensed Content Publication</td>
<td>Journal of Sol-Gel Science and Technology</td>
</tr>
<tr>
<td>Licensed Content Title</td>
<td>Zinc oxide nanowires in chemical bath on seeded substrates: Role of hexamine</td>
</tr>
<tr>
<td>Licensed Content Author</td>
<td>Abhilash Sugunan, Hemant C. Warad, Mats Boman et al</td>
</tr>
<tr>
<td>Licensed Content Date</td>
<td>Jan 1, 2006</td>
</tr>
<tr>
<td>Licensed Content Volume</td>
<td>39</td>
</tr>
<tr>
<td>Licensed Content Issue</td>
<td>1</td>
</tr>
<tr>
<td>Type of Use</td>
<td>Thesis/Dissertation</td>
</tr>
<tr>
<td>Requestor type</td>
<td>academic/university or research institute</td>
</tr>
<tr>
<td>Format</td>
<td>electronic</td>
</tr>
<tr>
<td>Portion</td>
<td>figures/tables/illustrations</td>
</tr>
<tr>
<td>Number of figures/tables/illustrations</td>
<td>1</td>
</tr>
<tr>
<td>Will you be translating?</td>
<td>no</td>
</tr>
<tr>
<td>Circulation/distribution</td>
<td>501 to 1000</td>
</tr>
<tr>
<td>Author of this Springer Nature content</td>
<td>no</td>
</tr>
<tr>
<td>Title</td>
<td>II-VI Semiconductor Nanowire Array Sensors Based on Piezotronic, Piezo-Phototronic and Piezo-Photo-Magnetotronic Effects</td>
</tr>
<tr>
<td>Instructor name</td>
<td>Shuke Yan</td>
</tr>
<tr>
<td>Institution name</td>
<td>University of New Orleans</td>
</tr>
<tr>
<td>Expected presentation date</td>
<td>Apr 2018</td>
</tr>
<tr>
<td>Order reference number</td>
<td>11</td>
</tr>
<tr>
<td>Portions</td>
<td>Figure 6</td>
</tr>
<tr>
<td>Requestor Location</td>
<td>Shuke Yan</td>
</tr>
<tr>
<td></td>
<td>2000 Lakeshore Dr.</td>
</tr>
</tbody>
</table>

NEW ORLEANS, LA 70148
United States
Attn: Shuke Yan

Billing Type | Invoice
Billing Address | Shuke Yan
               | 2000 Lakeshore Dr.
Terms and Conditions

Springer Nature Terms and Conditions for RightsLink Permissions

Springer Customer Service Centre GmbH (the Licensor) hereby grants you a non-exclusive, world-wide licence to reproduce the material and for the purpose and requirements specified in the attached copy of your order form, and for no other use, subject to the conditions below:

1. The Licensor warrants that it has, to the best of its knowledge, the rights to license reuse of this material. However, you should ensure that the material you are requesting is original to the Licensor and does not carry the copyright of another entity (as credited in the published version).

   If the credit line on any part of the material you have requested indicates that it was reprinted or adapted with permission from another source, then you should also seek permission from that source to reuse the material.

2. Where print only permission has been granted for a fee, separate permission must be obtained for any additional electronic re-use.

3. Permission granted free of charge for material in print is also usually granted for any electronic version of that work, provided that the material is incidental to your work as a whole and that the electronic version is essentially equivalent to, or substitutes for, the print version.

4. A licence for ‘post on a website’ is valid for 12 months from the licence date. This licence does not cover use of full text articles on websites.

5. Where ‘re-use in a dissertation/thesis’ has been selected the following terms apply:
   Print rights for up to 100 copies, electronic rights for use only on a personal website or institutional repository as defined by the Sherpa guideline (www.sherpa.ac.uk/romeo/).

6. Permission granted for books and journals is granted for the lifetime of the first edition and does not apply to second and subsequent editions (except where the first edition permission was granted free of charge or for signatories to the STM Permissions Guidelines http://www.stm-assoc.org/copyright-legal-affairs/permissions/permissions-guidelines/), and does not apply for editions in other languages unless additional translation rights have been granted separately in the licence.

7. Rights for additional components such as custom editions and derivatives require additional permission and may be subject to an additional fee. Please apply to Journalpermissions@springernature.com/bookpermissions@springernature.com for these rights.

8. The Licensor’s permission must be acknowledged next to the licensed material in print. In electronic form, this acknowledgement must be visible at the same time as the figures/tables/illustrations or abstract, and must be hyperlinked to the journal/book’s homepage. Our required acknowledgement format is in the Appendix below.

9. Use of the material for incidental promotional use, minor editing privileges (this does not include cropping, adapting, omitting material or any other changes that affect the meaning, intention or moral rights of the author) and copies for the disabled are permitted under this licence.

10. Minor adaptations of single figures (changes of format, colour and style) do not require the Licensor’s approval. However, the adaptation should be credited as shown in Appendix below.

Appendix — Acknowledgements:

https://is100.copyright.com/AppDispatchServlet
PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.

BACK  CLOSE WINDOW

Copyright © 2010 Copyright Clearance Center, Inc. All Rights Reserved. Privacy statement, Terms and Conditions.
Comments? We would like to hear from you. E-mail us at customerservice@copyright.com
VITA

The author of this work was born in China. He obtained his Bachelor’s degree in Metal Materials Engineering from Shijiazhuang Railway University, China, in 2005, Master’s degree in Materials Physics and Chemistry from University of Science and Technology Beijing, China, in 2008. After that, he worked in Nanjing Research Institute of Electronics Technology in China for one year. In 2012 he attended the Department of Chemistry at University of New Orleans and joined in Dr. Weilie Zhou’s research group. He received his second Master’s degree in Chemistry from University of New Orleans in 2016.