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ADVANCED NANOSTRUCTURED MATERIALS: WIDE-BAND-GAP OXIDES BASED MAGNETIC SEMICONDUCTORS

GUOZHONG XING

**DIVISION OF PHYSICS AND APPLIED PHYSICS
SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES
NANYANG TECHNOLOGICAL UNIVERSITY**

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Advanced Nanostructured Materials: Wide-Band-Gap Oxides Based Magnetic Semiconductors

GUOZHONG XING

School of Physical and Mathematical Sciences

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**To my wife, WANG Dandan
and my beloved parents,
who made everything possible**

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Abstract

Title of Dissertation: ADVANCED NANOSTRUCTURED MATERIALS:
 WIDE-BAND-GAP OXIDES BASED MAGNETIC
 SEMICONDUCTORS

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Dissertation directed by: Assistant Professor WU Tao, Tom (supervisor)

Assistant Professor SUM Tze Chien (co-supervisor)

Division of Physics and Applied Physics

Nanomaterials and Spintronics are focuses of research over the past ten years. The conjunction of electron spin with the charge manipulation in the semiconductor could lead to a whole new era in information technology, called semiconductor spintronics. It represents a new paradigm of accomplishing the functionalities of logic operation and data storage with high speed and low power consumption in next-generations of integrated magnetic sensors, transistors and lasers. The field of ferromagnetic semiconductors is dominated by Japan, rapidly advanced in United States and highlighted as an important emerging technology across continental Europe. Until recently, Singapore research groups have played a minor role in the field of ferromagnetic semiconductors. Semiconductor spintronics has already become a major research area. Spintronics is very likely to have a significant impact on future generations of devices.

Operation of spintronic devices could consume much less energy because aligning spins is more efficient than redistributing charges. The discovery of ferromagnetic ordering in wide-band-gap semiconductors generated tremendous attention by the theoretical prediction that Mn doped *p*-type ZnO would show room temperature ferromagnetism (RTFM). Interestingly, over the past years, it has been well recognized that the major obstacle in studying the magnetism in dilute doped oxides is related to extrinsic tendency of metal clustering. The resulting attractive force between the magnetic cations leads to their aggregation, invalidating the main promise of diluted magnetic semiconductors (DMSs) and diluted magnetic oxides (DMOs) especially. Accordingly, initiating from the d^0 magnetism observation addressed in 2005 by J. M. D. Coey *et al.* in undoped oxide systems, the demanding properties investigation of both DMSs and DMOs are emergent. Typically, as the extensively studied systems, wide-band-gap-oxides, e.g. ZnO and In₂O₃-based DMOs show Curie temperature (T_c) well above room temperature, and promising magneto-optical and magnetotransport characteristics. Steady progress is being made on this front, but recent reports demonstrate that progress is far from dormant. This is very demanding, because they have vital impact on the fundamental research development and practical application of DMOs.

The main objective of this dissertation is to extend the understanding of origin and mechanisms of the observed FM in wide-band-gap oxide based semiconductors and to achieve the controlled synthesis of functional nanocomposites with defined morphologies and properties, which are potential candidates as building blocks for future spintronics nanodevices.

In this dissertation, I studied the fabrication and performance investigations of two

typical wide-band-gap oxide nanocomposites, i.e., Zinc Oxide, Indium Oxide and their doped counterparts, using conventional synthesis routes, e.g., a simple method of vapor transport deposition and the atomic layer deposition technique. Various nanocomposites (e.g. nanowires, core/shell heterostructures and nanotowers *etc.*) were obtained. Their structures and physical properties, especially magnetic characteristics could be modulated by chemical compositions, growth mechanisms, and other experimental parameters, which further suggests that the defects evolution/engineering may one day pave the way for the promotion and development of DMOs-based spintronics research community.

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List of Publications

1. Wang, Dandan*; Chen, Qian*; **Xing GZ***; Yi, Jiabao; Rahman, Saidur; Ding, Jun; Wang, Jinlan; Wu, Tom, "Robust Room-Temperature Ferromagnetism with Giant Anisotropy in Nd-Doped ZnO Nanowire Arrays", *Nano Letters* 12, 3994 (2012)
2. **Xing GZ**, Yunhao Lu, Yufeng Tian, Jiabao Yi, C. C. Lim, Yongfeng Li, Gongping Li, Dandan Wang, Bin Yao, Jun Ding, Yuanping Feng, and Tom Wu "Defect-induced magnetism in wide band gap oxides: zinc vacancies in ZnO as an example" *AIP Advances* 1, 022152 (2011)
3. V. Thakare*, **Xing GZ***, Haiyang Peng, A. Rana, O. Game, P. Anil Kumar, A. Banpurkar, Y. Kolekar, K. Ghosh, Tom Wu, D. D. Sarma, and S. B. Ogale, "High Sensitivity Low Field Magnetically Gated Resistive Switching in $\text{CoFe}_2\text{O}_4/\text{La}_{0.66}\text{Sr}_{0.34}\text{MnO}_3$ Heterostructure" *Appl. Phys. Lett.* 100, 172412 (2012)
4. **Xing GZ**, Dandan Wang, Jiabao Yi, Lili Yang, Ming Gao, Mi He, Jinghai Yang, Jun Ding, T. C. Sum, and Tom Wu, "Correlated d^0 Ferromagnetism and photoluminescence in undoped ZnO Nanowires" *Appl. Phys. Lett.* 96, 112511 (2010)
5. **Xing GZ**, Xiaosheng Fang, Zhou Zhang, Dandan Wang, Xiao Huang, Jun Guo, Lei Liao, Zhe Zheng, Hairuo Xu, Ting Yu, Zexiang Shen, C. H. A. Huan, T. C. Sum, Hua Zhang, and Tom Wu, "Ultrathin single-crystal ZnO nanobelts: Ag-catalyzed growth, optical absorption and field emission properties" *Nanotechnology* 21, 255701 (2010)
6. **Xing GZ**, Jiabao Yi, Dandan Wang, Lei Liao, Ting Yu, Zexiang Shen, T. C. Sum, Jun Ding, and Tom Wu, "Strong Correlation between Ferromagnetism and Oxygen Deficiency in Cr-doped $\text{In}_2\text{O}_{3-\delta}$ Nanostructures" *Phys. Rev. B* 76, 174406 (2009)
7. **Xing GZ**, Jiabao Yi, Junguang Tao, Tao Liu, L. M. Wong, Zhou Zhang, Gongping Li, Shijie Wang, Jun Ding, T. C. Sum, C. H. Alfred Huan, and Tom Wu, "Comparative study of structural inhomogeneity enhanced room-temperature Ferromagnetism in Cu-doped ZnO nanowires" *Adv. Mater.* 20, 3521 (2008)
8. **Xing GZ**, Junguang Tao, Gongping Li, Zhou Zhang, L. M. Wong, Shijie Wang, C. H. Alfred Huan and Tom Wu, "Doping Cu into ZnO Nanostructures" *IEEE International Nanoelectronics Conference*, 1-3, 462 (2008)
9. **Xing GZ**, S. T. Ali, K. Michael, J. S. Edbert, Dandan Wang, Faxin Zang, Zhipeng Wei,

- C. H. Alfred Huan, Tom Wu and T. C. Sum, “Ultrafast Optical Studies in Transition-Metal-Doped ZnO NWs” *ICMAT & IUMRS-ICA 2009*, Singapore
10. **Xing GZ**, Yi Jiabao, Wang Dandan, Liao Lei, Yu Ting, Shen Zexiang, Alfred Huan, Sum TC and Tom Wu, “Bound Magnetic Polarons Induced FM in Transition-Metal-Doped Oxide Nanostructures” *IEEE International Nanoelectronics Conference*, 1-2, 1120 (2010)
 11. **Xing GZ**, Guichuan Xing, Mingjie Li, Edbert Jarvis Sie, Dandan Wang, Arief Sulistio, Quanlin Ye, Cheng Hon Alfred Huan, Tom Wu and Tze Chien Sum “Charge Transfer Dynamics in Cu-doped ZnO NWs” *Appl. Phys. Lett.* 98, 102105 (2011)
 12. Dandan Wang*, **Xing GZ***, Ming Gao, Zhou Zhang, Lili Yang, Jinghai Yang and Tom Wu, “Efficient Room-Temperature Defect-Assisted Energy Transfer in Eu-Doped ZnO Nanowire Arrays” *J. Phys. Chem. C* 115, 22729 (2011)
 13. **Xing GZ**, Guichuan Xing, Dandan Wang, Rui Chen, Handong Sun, C. H. Alfred Huan, Tom Wu and T. C. Sum “Highly Spin-polarized Excitonic Emission in Cu-doped ZnO Nanowires” (In preparation)
 14. **Xing GZ**, Dandan Wang, C.-J. Cheng, T. C. Sum and Tom Wu “Interface Induced FM in ZnO Nanowires” (In preparation)
 15. Jiabao Yi, C. C. Lim, **Xing GZ**, Haiming Fan, L. H. Van, Shengli Huang, K. S. Yang, X. L. Huang, X. B. Qin, B.Y. Wang, Tom Wu, Lan Wang, H. T. Zhang, X.Y. Gao, T. Liu, A. T. S. Wee, Yuanping Feng, and Jun Ding “Ferromagnetism in Dilute Magnetic Semiconductors through Defect Engineering: Li-doped ZnO” *Phys. Rev. Lett.* 104, 137201 (2010)
 16. Huatao Wang, J. C. Wu, Y. Q. Shen, Gongping Li, Zhou Zhang, **Xing GZ**, D. L. Guo, Dandan Wang, Z. L. Dong and T. Wu, “CrSi₂ Hexagonal Nanowebs” *J. Am. Chem. Soc.* 132, 15875 (2010)
 17. T. Kataoka, Y. Yamazaki, A. Fujimori, **Xing GZ**, J. W. Seo, C. Panagopoulos, and Tom Wu, “Ferromagnetic interaction between Cu ions in the bulk region of Cu-doped ZnO Nanowires” *Phys. Rev. B* 84, 153203 (2011)
 18. Dandan Wang, **Xing GZ**, Haiyang Peng, and Tom Wu, “Chlorine-assisted size-controlled synthesis and tunable photoluminescence in Cr-doped silica nanospheres” *J. Phys. Chem. C* 113, 7065 (2009)

19. Dandan Wang, Jinghai Yang, **Xing GZ**, Lili Yang, Jihui Lang, Ming Gao, Bin Yao, and Tom Wu, “Abnormal blueshift of UV emission in single-crystalline ZnO Nanowires” *J. Lumin.* 129, 996 (2009)
20. Tao Chen, **Xing GZ**, Zhou Zhang, Hongyu Chen, Tom Wu, “Tailoring the photoluminescence in ZnO NWs using Au nanoparticles” *Nanotechnology* 19, 435711 (2008)
21. Rui Chen, **Xing GZ**, Jing Gao, Zhou Zhang, Tom Wu and H. D. Sun, “Characteristics of ultraviolet photoluminescence from high quality tin oxide Nanowires” *Appl. Phys. Lett.* 95, 061908 (2009)
22. Donglai Guo, Xiao Huang, **Xing GZ**, Zhou Zhang, Gongping Li, Mi. He, Hua Zhang, Hongyu Chen, and Tom Wu “Metal-layer-assisted coalescence of Au nanoparticles and its effect on diameter control in vapor liquid solid growth of oxide Nanowires” *Phys. Rev. B* 83, 045403 (2011)
23. Kewei Liu, Rui Chen, **Xing GZ**, Tom Wu and Handong Sun, “Photoluminescence characteristics of high quality ZnO NWs and its enhancement by polymer covering” *Appl. Phys. Lett.* 96, 023111 (2010)
24. Lei Liao, Bin Yan, Y. F. Hao, **Xing GZ**, Jinping Liu, Zexiang Shen, Ting Wu, Lan Wang, J. T. L. Tong, Changmin Li, W. Huang, and Tom Yu, “P-type electrical, photoconductive, and anomalous ferromagnetic properties of Cu₂O NWs” *Appl. Phys. Lett.* 94, 113106 (2009)
25. Lei Liao, Bin Yan, Zhou Zhang, L. L. Chen, B. S. Li, **Xing GZ**, Zexiang Shen, Tom Wu, Xiaowei Sun, J. Wang, and Ting Yu, “ZnO NW transistor: a nonvolatile ferroelectric memory” *ACS NANO* 3, 700 (2009)
26. Huatao Wang, Zhou Zhang, L. M. Wong, Shijie Wang, Zhipeng Wei, **Xing GZ**, Donglai Guo, Dandan Wang, and Tom Wu, “Morphology-controlled formation of nanopits on silicon substrates via nanoscale silicide sublimation” *ACS NANO* 4, 2901 (2010)
27. Wei Zhipeng, Arredondo M, Peng Haiyang Zhang Zhou, Guo Donglai, **Xing GZ**, Li Yongfeng, Wong LM, Wang Shijie, Valanoor N, Wu Tom “A Template and Catalyst

- Free Metal Etching Oxidation Method to Synthesize Aligned Oxide NW Arrays: NiO as an Example” *ACS NANO* 4, 4785 (2010)
28. Zhou Zhang, Jing Gao, Lei Liao, Zhe Zheng, **Xing GZ**, Haiyang Peng, Ting Yu, Zexiang Shen, C. H. Alfred Huan, Shijie Wang, and Tom Wu, “Morphology controlled synthesis and comparative study of physical properties of SnO₂ nanostructures: from ultrathin NWs to ultrawide nanobelts” *Nanotechnology* 20, 135605 (2009)
 29. Yingrui Sui, Bin Yao, Zhong Hua, **Xing GZ**, X. M. Huang, Tong Yang, Lili Gao, Tingting Zhao, Huilin Pan, H. Zhu, W. W. Liu, Tom Wu, “Fabrication and properties of B-N codoped *p*-type ZnO thin films” *J. Phys. D: Appl. Phys.* 42, 065101 (2009)
 30. Huiying Yang, S. F. Yu, S. P. Lau, S. H. Tsang, **Xing GZ**, Tom Wu, “Ultraviolet coherent random lasing in SnO₂ Nanowires” *Appl. Phys. Lett.* 94, 241121 (2009)
 31. Zhou Zhang, Jiabao Yi, Jun Ding, L. M. Wong, H. L. Seng, S. J. Wang, Junguang Tao, Gongping Li, **Xing GZ**, T. C. Sum, C. H. Alfred Huan, and Tom Wu, “Cu-doped ZnO nanoneedles and nanonails: morphological evolution and physical properties” *J. Phys. Chem. C* 112, 9579 (2008)
 32. Peng Haiyang, Li Gongping, Ye Jiaying, Wei Zhipeng, Zhang Zhou, Wang Dandan, **Xing GZ**, Wu Tom “Electrode dependence of resistive switching in Mn-doped ZnO: Filamentary versus interfacial mechanisms” *Appl. Phys. Lett.* 96, 192113 (2010)
 33. Rui Chen, Y. Tay, J. Ye, Y. Zhao, **Xing GZ**, Tom Wu and Handong Sun, “Investigation of Structured Green Band Emission and Electron-Phonon Interactions in Vertically Aligned ZnO NWs” *J. Phys. Chem. C* 114, 17889 (2010)
 34. Yongfeng Li, Rui Deng, Bin Yao, **Xing GZ**, Dandan Wang and Tom Wu, “Tuning FM in Mg_xZn_{1-x}O thin films by band gap and defect engineering” *Appl. Phys. Lett.* 97, 102506 (2010)
 35. Shichen Su, Youming Lv, **Xing GZ** and Tom Wu, “Spontaneous and stimulated emission of ZnO/Zn_{0.85}Mg_{0.15}O asymmetric double quantum wells” *Superlattices and Microstructures* 48, 485 (2010)
 36. Xiaohu Huang, Z. Y. Zhan, X. Wang, Zhou Zhang, **Xing GZ**, Donglai Guo, D. P. Leusink, L. X. Zheng and Tom Wu "Rayleigh-Instability-Driven Transformation from Co NWs to CoO Octahedra" *Appl. Phys. Lett.* 97, 203112 (2010)

37. Chenliang Lu, Y. Wang, Lu You, X. Zhou, Haiyang Peng, **Xing GZ**, E. E. M. Chia, C. Panagopoulos, Lang Chen, J. M. Liu, J. L. Wang, and Tom Wu “Superconducting gap induced barrier enhancement in a BiFeO₃-based heterostructure” *Appl. Phys. Lett.* 97, 252905 (2010)
38. Yimin Cui, S. Yin, Dandan Wang, **Xing GZ**, S. H. Leng, and Rongming Wang “Electrical characteristics of Au and Ag Schottky contacts on Nb-1.0 wt %-doped SrTiO₃” *J. Appl. Phys.* 108, 104506 (2010)
39. Tong Yang, Bin Yao, Tingting Zhao, **Xing GZ**, H. Wang, Huilin Pan, Rui Deng, Yingrui Sui, L. L. Gao, Haizhu Wang, T. Wu and D. Z. Shen “Sb doping behavior and its effect on crystal structure, conductivity and photoluminescence of ZnO film in depositing and annealing processes” *J. Alloys Compd.* 509, 5426 (2011)
40. Mi He, Yufeng Tian, Daniel Springer, I. A. Putra, **Xing GZ**, E. E. M. Chia, S. A. Cheong, Tom Wu, “Polaronic transport and magnetism in Ag-doped ZnO” *Appl. Phys. Lett.* 99, 222511 (2011)
41. Mingjie Li, Guichuan Xing, L. F. N. A. Qune, **Xing GZ**, Tom Wu, C. H. Alfred Huan, Xinhai Zhang, T. C. Sum, “Tailoring the charge carrier dynamics in ZnO NWs: the role of surface hole/electron traps” *Phys. Chem. Chem. Phys.* 14, 3075 (2012)
42. Bingye Zhang, Bin Yao, Yongfeng Li, A. M. Liu, Zhenzhong Zhang, **Xing GZ**, Tom Wu, X. B. Qin, Dongxu Zhao, Chongxin Shan, and Dezhen Shen “Evidence of cation vacancy induced room temperature FM in Li-N codoped ZnO thin films” *Appl. Phys. Lett.* 99, 182503 (2011)
43. Lili Yang, Qingxiang Zhao, **Xing GZ**, Dandan Wang, Tom Wu, M. Willander, I. Ivanov, Jinghai Yang, “A SIMS study on Mg diffusion in Zn_{0.94}Mg_{0.06}O/ZnO heterostructures grown by metal organic chemical vapor deposition” *Applied Surface Science* 257, 8629 (2011)

Chapter 1 Introduction

§1.1 Background and challenges

The conjunction of electron spin with charge manipulation in the semiconductor could lead to a new era in information technology field, called semiconductor spintronics. *Spintronics* utilizes not only charges but also spins to process, store, and transmit information, creating functionalities difficult or even inaccessible for the conventional semiconductor technologies.¹ Compared to the conventional electronics, spintronics offers advantages like non-volatility, high speed memory and low power consumption, all related to the intrinsic nature of spin manipulation. Operation of spintronic devices could consume much less energy because aligning spins is more efficient than redistributing charges. Furthermore, spintronic devices are intrinsically nonvolatile, which, for example, helps to maximize the battery lifetime for mobile devices.

The mechanism of spintronic devices is intrinsically different from their conventional counterparts. The main driving force behind the current magnetoelectronics studies is the persistently demanding for higher record densities, which requires the use of high sensitivity read sensors. As shown schematically in **Figure 1-1**, is a simplest spin-valve (SV), one of prototype spintronics devices, that consists of two ferromagnetic layers separated by a non-magnetic spacer; one of which is free to switch between parallel and antiparallel alignments corresponding to the low and high resistivity states, respectively. Current perpendiculars to plane sensors are being studied as a next

generation sensors because of their suitability for further downsizing.

Figure 1-1. Schematic illustration of a simple spin-valve device structure.

Figure 1-2. Calculated results of the T_C for various p -type semiconductors containing 5% of Mn and 3.5×10^{20} holes/cm³ [Ref. 2].

The initial sighting of FM in Mn-doped narrow band gap semiconductors has attracted tremendous attention. However, diluted magnetic semiconductor materials such as GaMnAs and GaMnSb, have thus far shown relatively low magnetic ordering temperatures (~ 170 K for GaMnAs), which confines their applications. Recently, many research groups reported on achieving FM at or above RT in wide-band-gap materials, such as GaMnN and ZnMnO following the pioneering report by Dietl *et al.*² as shown in

Figure 1-2. This report has been followed by numerous experiments on RTFM in ZnO doped with wide range transition metals. However, large controversies also originate from the fact that the observed FM is usually so weak that it is hard to distinguish it from the extrinsic sources or experimental artefacts.

Acting as potential magnetic spin aligner host, both ZnO and In_2O_3 are good candidates. ZnO is a wide-band-gap (~ 3.37 eV) oxide semiconductor, it has been a focus of intensive interest most recent years.³ The unparalleled features of ZnO for optoelectronic applications, in addition to its wide-band-gap similar to that of GaN, are its high exciton binding energy (60 meV) and the availability of bulk ZnO single crystals.⁴ More advantages of ZnO are that it can be easily processed by wet chemical etching and also it possesses excellent stability even under a high-energy radiation. Furthermore, it can be synthesized with a lot of nanostructured morphologies by using low cost and low temperature methods.⁵ ZnO is also promising in achieving high spin polarized injection efficiencies and carriers due to the 3d-transition metals have relatively high solubility (up to $\sim 35\%$ for Mn and Co).⁶ Importantly, spin orbit coupling strength is fairly small in ZnO because the valence-band splitting is ~ 3.5 meV.⁷ In theory, the smaller spin orbit coupling should lead to long spin relaxation time, which is required if spin information is to be transported over appreciable distances. All of these potential advantages stimulate intense research interest in ZnO.⁸

Recently, there has been accumulating evidences suggesting that defects play important roles in establishing the magnetic order in wide-band-gap oxides. In particular, RTFM has been reported in undoped ZnO, which to a certain degree helps to settle the controversies delineated above due to the absence of any intentionally doped metallic

element. This emergent FM in undoped oxides is often called ‘ d^0 FM’, where defects are believed to be responsible for initiating the hybridization at the Fermi level and establishing a long range FM. However, open questions still remain related to this approach of defect engineering towards magnetism in oxides: e.g., what kinds of defects can contribute magnetic moments? How to establish the long-range magnetic coupling of local moments in an oxide host? Thus, it is of paramount important to investigate the roles of intrinsic defects in the onset of FM because of their abundance in wide-band-gap oxides.

Analogous to the ZnO system, another wide-band-gap oxide system, In_2O_3 forms in a cubic bixbyite crystal structure, with the direct band-gap of ~ 3.75 eV. Films of In_2O_3 are superior to other transparent conductors, largely due to their higher mobility, $10\sim 75\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, with a carrier density of $10^{19}\sim 10^{20}$ electrons cm^{-3} .^{9, 10} Importantly, a T_c of ~ 850 K was reported on Cr-doped In_2O_3 thin films sparked studies in this wide-band-gap oxide based DMO systems.¹¹ As the extensively studied systems, wide-band-gap oxide ZnO and In_2O_3 based diluted magnetic oxides (DMOs) show T_c well above RT,^{12, 13} and promising magneto-optical¹⁴ and magnetotransport characteristics.^{11, 15} Steady progress is being completed on this front, but few works have been carried out on the spin-polarized transport in homojunction made from doped-ZnO and recent reports demonstrate that progress is far from dormant. This is highly demanding, because they not only have an impact on the application of DMOs but also provide information for spin injection. The spin injection, transportation and detection from doping ZnO layer to pure ZnO and other conventional semiconductors is an important long term goal of proceeding research in ZnO DMOs.¹²⁻¹⁶ Clearly, there is a pressing need for spin-based devices comprising of

DMOs with high T_c and spin polarization (P_s) to enhance the operation temperature and elevate spin injection efficiency then eventually to achieve RT devices paradigm.

Transition metals (TM) doped wide-band-gap oxides offer an unprecedented opportunity for considering physical phenomena and device concepts for previously unavailable combination of quantum structures and FM in semiconductors.¹⁷ The presence of magnetic ions such as TM ions in diluted magnetic semiconductors tends to have an exchange interaction between itinerant sp band electrons or holes and the d electrons spins localized at the magnetic ions, resulting in versatile magnetic field induced functionalities. Transition metals or rare earths doped oxide materials with typically wide band gaps are attracting growing attention. Consequently, how to increase the doping efficiency and dopant solubility in host without presence of clusters and precipitates warrants the urgent studies. As well known, doping is a widely used means to tailor the band structures of bulk semiconductors, facilitating the construction of various devices essential for the development of microelectronics. For device integration with high density and complementary functionalities, developing appropriately doped wide-band-gap oxide semiconductor nanostructures is of fundamental significance. Furthermore, in some cases, doped nanostructures are promising to exhibit better performance than the bulk counterparts. The ability to modulate the fundamental electronic properties of nanostructures through doping has been a central issue in developing active electronic and optoelectronic nanodevices, where the composition and/or doping is modulated down to the atomic level. Although the importance of selecting precursor materials is well known, the efficiency of transferring dopants into the nanostructures during their growth is hard to predict if not impossible.¹⁸ Therefore, I

focused on developing various strategies and investigating their individual advantages for specific applications.

§1.2 Motivation

Spintronics is emerging as a hot research field and a novel technology building on generating, manipulation, and detection of not only charges, but also spins. The first generation of spintronic devices as read-out heads for computer hard drives have achieved huge commercial success and developed into a market worth billions of dollars per year. Exploring the advantages spintronic devices could offer new solution to overcome the difficulties experienced by conventional electronics as the device dimension goes into the nano-regime, therefore providing potential candidates for next-generation sustainable electronic applications.

Oxide semiconductors are environmental-friendly materials and possess diverse novel electrical, magnetic and optical properties. Exploration of new diluted magnetic wide-band-gap oxide semiconductors may lead to evolution of some important spintronic devices. Bandgap engineering by novel doping in high quality nanowires (NWs) are expected to significantly advance this field. This research is of vital importance due to not only the new physics, but also the pressing need to scale down the dimension of spintronic devices in next generation technologies.

Although there have been intensive efforts on oxide semiconductors, the research on spintronic wide-band-gap oxides is still at a preliminary stage. There is therefore an urgent need to develop new strategies to make high-quality epitaxial nanocomposites and

NWs of spin-polarized materials. However, the progress has been hampered by large disparities in experimental results and interpretations. Thus, it is of paramount importance to investigate the roles of intrinsic defects in the onset of FM because of their abundance in wide-band-gap oxides. On the other hand, we should note that the strong influence of TM doping on the magnetic characteristics of oxide magnetic semiconductors. Furthermore, there remain many open questions regarding the dynamics of charges and spins in the diluted magnetic wide-band-gap oxides based spintronic devices. Efficient electrical spin injection, spin transport, and spin detection have to be achieved in order to realize high performance spintronic devices.

§1.3 Objectives

In this dissertation, I seek to study advanced nanostructured wide-band-gap oxides based magnetic semiconductors via novel synthesis and doping strategies. Nanoscale geometric confinement often brings about new properties via effects of reduced dimensionality, large surface-to-volume ratio, modulated strain state, discrete energy levels, and so on.¹⁹ One-dimensional nanomaterials, especially NWs, have become the focus of intensive research owing to their unique applications as both interconnects and functional units in electronic, electrochemical, optoelectronic and electromechanical devices. As an example, aligned ZnO NWs were demonstrated as RT nanolasers with surface-emitting action at ultraviolet wavelength.²⁰ The richness of this bottom-up approach also manifests in works from Prof. Charles Lieber's group on electronic, chemical and biological sensing devices based on NWs of Si and other semiconductor

materials.¹⁹ I also propose a systematic in-depth investigation of a new paradigm of using wide-band-gap oxide NWs as the bottom-up building blocks for constructing spintronic devices.

My dissertation will focus on two important aspects: one is to develop novel synthesis and doping strategies in magnetic wide-band-gap oxides; the other is to systematically investigate the physical properties of these multifunctional materials. In this thesis, I synthesized and characterized wide-band-gap oxide materials with stable magnetic ordering and high spin polarization. I also aim to use these novel materials to construct advanced functional spin valves to understand the charge and spin dynamics, which will be highly relevant to their potential applications in spintronic devices.

§1.4 Organization of the thesis

During my Ph.D. studies, I have synthesized different kinds of undoped and TM elements doped oxide one dimensional (1D) nanostructures such as Zinc Oxide and Indium Oxide nanowires successfully. Moreover, the physical properties have been investigated such as magnetic and optical properties, which show great potential applications in spintronic devices. Our team has expertise in experimental NW synthesis and nanodevice construction. **Figure 1-3** shows examples of our recent works on the RTFM of magnetic oxide semiconductors, i.e., Cu-doped ZnO NWs, undoped ZnO NWs and Cr-doped $\text{In}_2\text{O}_{3-\delta}$ nanostructures. These works have been recognized by the research community and our papers have been published in *Advanced Materials*,²¹ *Applied Physics Letters*²² and *Physical Review B*,²³ etc. and have attracted a number of citations.

Figure 1-3. Representative accomplished works related to the two main materials categories which I will present in this dissertation. (a) Magnetization vs. magnetic field data for two types of Cu-doped ZnO NWs synthesized in our laboratory. Compared with the NWs with homogeneous Cu doping, the NWs with stronger structural inhomogeneity show much enhanced magnetism at room temperature.²¹ (b) $M-H$ loops of three diverse undoped ZnO NWs taken at 5 and 300 K. The inset is the plot of RT saturation magnetizations and green band/UV emission ratios of three types of NW vs. the corresponding oxygen deficiency levels.²² (c) Cr-doped In_2O_3 nanotowers (CIO-T1), NWs (CIO-W1) and octahedrons (CIO-O1) were prepared using a vapor transport method. Strong RTFM was observed in the as-grown oxygen-deficient samples.²³

The dissertation begins with Chapter 1, which describes the background and challenges, motivation and objectives of the research. The organization of the thesis is also presented in this chapter. The fundamental concepts, basic principle of the spintronics and DMS/DMO materials have been reviewed. At the end of this chapter, the state-of-art of the ZnO and In_2O_3 based DMOs, in particular Cu:ZnO, undoped ZnO and Cr: In_2O_3 are illustrated in details.

Chapter 2 describes the fabrication methods and characterization approaches adopted in this work.

The mechanism and physical origin of FM in undoped ZnO NWs and core/shell type NWs are the essences of Chapter 3. The role of intrinsic defects in the ferromagnetic undoped ZnO NWs and core/shell type NWs are studied.

Chapter 4 provides the detailed fabrication and characterization of Cu-doped ZnO NWs. The systematical studies of structure, FM origin and spin polarization in Cu-doped ZnO NWs were carried out. The bound magnetic polarons (BMP) model was investigated for further understanding of observed magnetic properties in Cu-doped ZnO NWs. The possible mechanism of the enhanced FM and spin polarization degree are proposed.

Chapter 5 designates the strong correlation between oxygen deficiency and FM in diverse Cr-doped $\text{In}_2\text{O}_{3-\sigma}$ nanostructures. The detailed fabrication and optical and magnetic properties of the Cr-doped $\text{In}_2\text{O}_{3-\sigma}$ nano-towers, NWs and octahedrons are studied.

The dissertation ends in Chapter 6 with a summary of the main conclusions and recommendations for the further research.

Chapter 2 Experiments and Methodologies

§2.1 Conventional Nanocomposites Synthesis Routes

§2.1.1 Chemical Vapor Deposition (CVD)

A variety of methods have been developed to produce nanostructures, such as electrodeposition, sol-gel, and polymeric filter membranes assisted deposition, *etc.*²⁴⁻³⁰ These methods provide the possibility of forming oxide nanostructures at low temperature. But, such methods have to be involved with the anodic alumina membranes (AAM) as a template and be immersed into the suspension containing acid salts, then the preformed nanowire array requires to be oxidized at a temperature range of 120 to 300 °C for 2 to 6 hours, eventually the nanowire array can be obtained. These methods are complementary to the vapor transport synthesis of oxide nanostructure. However, the wet chemicals and/or AAM template have to be employed in the above mentioned methods for assistance to produce the final nanowires, consequently such procedure will induce nontrivial surface effects and unintentional contamination with relatively low crystal quality, sometime even lead to amorphous phase formation. In contrast, the most common one to synthesize oxide nanostructures utilizes a vapor transport process, i.e., chemical vapor transport deposition (CVD), and it has been very successful and versatile in fabricating high crystal quality 1-D oxide nanostructures with various physical and chemical characteristics.³¹⁻³³ The basic process of this technique is sublimating source materials in a powder form at a certain temperature, and in a particular temperature region a subsequent deposition of the vapor to form the desired nanostructures.

Figure 2-1. Schematic illustration of the vapor transport experimental setup for common oxide nanostructures growth.

A typical nanostructures fabrication setup is shown in **Figure 2-1**. The synthesis is performed in a quartz tube which is located in a horizontal tube furnace. High purity oxide powders mixed with graphite with particular weight ratio contained in an alumina boat are placed in the middle of the furnace. The substrates, which are coated with a metal catalyst of a certain thickness (Au, Ag and Pt *etc.*) for collecting the desired nanostructures, are usually located downstream following the carrier gas. The substrates we used are Silicon (Si), Al_2O_3 (Sapphire), SrTiO_3 (STO) and Indium-Tin-Oxide (ITO) coated quartz with different orientations. Both ends of the tube are covered by stainless steel clamps and sealed with O-rings.³⁴

During the experiments, the quartz tube is first pumped down to $\sim 10^{-2}$ mbar. Then the furnace is initiated to heat the tube to the reaction temperature at a specific heating rate (normally at $20^\circ\text{C}/\text{min}$). The carrier gas, such as Ar or Ar mixed certain percentage of O_2 , is then introduced into the system at a constant flow rate [10 to 100 standard cubic centimeter per minute (sccm)]. The inner pressure was kept at around few tens of mbar. The reaction temperature and pressure are kept constant for a certain period of time to vaporize the source material and achieve a reasonable amount of deposition. Source

materials can be vaporized at the high temperatures and low pressure condition. The vapor is then transferred by the carrier gas down to the lower temperature region, where the vapor gradually becomes supersaturated. Once it reaches the substrate, nucleation and growth of nanostructures will occur.³⁵ The system is then cooled down to RT naturally with flowing of an inert gas. To obtain an accurate estimation of the growth temperature, the temperature gradient of the tube furnace was calibrated using a thermocouple.

Taking ZnO nanostructures synthesis as an example, in such vapor transport process, Zn and O₂ or O₂ mixture vapor are transported and react with each other, forming ZnO nanostructures. Should dopants need to be incorporated during the synthesis, the associated dopant source, usually oxide compounds, will be mixed with host oxide powder and then ground with graphite powder.

By tuning the experimental conditions, such as growth temperature, oxygen concentration, gas flow rate and working pressure, the nanostructures growth can be well controlled. During my PhD studies, I had successfully synthesized several kinds of Zinc Oxide and Indium Oxide nanostructures. In a typical synthesis process, ZnO mixed with graphite as the source powders were loaded in a certain position of a horizontal quartz tube furnace. The commercially available substrates were carefully cleaned in organic solvents and acids to remove residual contaminations, then coated with catalyst Au or Ag thin film (or nanoparticles) and were placed in the downstream from the mixed powder source. The inner pressure of quartz tube was maintained by regulating the gas flow rate and tuning the valve of a mechanical pump. During the heating, ZnO is reduced by graphite and gives out Zn vapor. Carrier gas (e.g., a few fractions O₂ mixed Ar) is introduced and carries Zn vapor to the substrate region where it is then absorbed by the

catalyst to form a certain alloy, when this kind of alloy becomes supersaturated and the condensation is subsequently oxidized to form the ZnO nanostructures. So far, ZnO NWs, nanorods, nanoneedles, nanobelts, nanotubes and many other fantastic nanostructures have been successfully synthesized via this technique throughout all experiments during my PhD study.

Figure 2-2. Schematic NWs growth progress under VLS and VS mechanisms.

It is well known that the nanostructures growth is usually dominated by the vapor liquid solid (VLS) and the vapor solid (VS) mechanism via chemical vapor deposition method,³³ as shown in **Figure 2-2**. In VLS mechanism,³⁶ source vapor is absorbed and dissolved in liquid catalyst nanoparticles until it becomes supersaturated which leads to the precipitation and the growth of NWs at the interface between the substrate and the liquid nanoparticles. The advantage of VLS process is that the NWs diameter can be precisely defined by the catalyst size. NWs can also grow without catalyst through the VS mechanism due to different growth rates at different crystal orientations or preferential accumulation of impurities as the nucleation centers. VLS and VS mechanisms usually occur simultaneously and compete with each other. In my experiments, the nanostructures growth can be controlled very well by optimizing the experimental conditions and

physical parameters, which is very important for the following physical properties investigations and potential device applications.

§2.1.2 Atomic Layer Deposition (ALD)

The idea of the ALD process was first proposed by Professor V. B. Aleskovskii in 1952.³⁷⁻³⁹ ALD is a typical and unique thin film deposition technique which utilizes chemicals, i.e., precursors. Such precursors can react with a surface one at a time in a sequential manner. A thin film can be formed by exposing the precursors to the growth surface repeatedly.⁴⁰ ALD deals with precise control of depositions at the atomic scale, it can be employed to deposit a variety of thin films, including various oxides, such as ZnO, Al₂O₃, SnO₂, TiO₂, HfO₂, metal nitrides, e.g., TiN, WN, NbN, TaN, metals, e.g., Ir, Pt, Ru, and metal sulfides, e.g., ZnS.

Using ALD, the film thickness is only dependent on the reaction cycles, which facilitates simple and accurate control of the thickness. The growth of different multilayer structures is straightforward. In my experiments, as to the ZnO/Al₂O₃ core/shell heterostructure synthesis, the Si substrates covered with as-grown ZnO NWs were first transferred to the ALD chamber (Cambridge, Nanotech Savannah 100) and prebaked in vacuum ($\sim 1.5 \times 10^{-1}$ torr) at 200 °C for 1 h with a constant Ar flowing of 10 sccm. Then Al₂O₃ deposition occurred at 200 °C using trimethylaluminum [Al(CH₃)₃] and water as the Al and oxygen source, respectively. Each cycle consisted of a 1.3 s pulse precursor, 20 s exposure time and 1 min Ar purging time. The thickness of the Al₂O₃ shell is controlled by the number of precursor cycles. In my study, a total number of 65 cycles was used,

which yields an alumina thickness of 10.0 ± 0.3 nm as measured from TEM experiments. This corresponds to an average growth rate for Al_2O_3 of $1.5 \text{ \AA/cycle}$. The sample of $\text{ZnO}/\text{Al}_2\text{O}_3$ core/shell NWs was then annealed in air at $\sim 700^\circ\text{C}$ for 3 hours to activate the interfacial solid-state reaction.

§2.2 Samples Characterization Methodology

§2.2.1 X-ray Diffraction (XRD)

XRD technique had been used for the fingerprint characterization of numerous crystalline materials and the determination and investigation of their structures.⁴¹ Every crystalline solid has its unique characteristic x-ray powder pattern features which can be utilized as the "fingerprint" for its crystal structure identification. Once the material has been identified, x-ray crystallography can be employed to determine its structure, i.e., how the atoms pack together in the crystalline state with a certain orientation and what the interatomic distance and angle are *etc.* When the certain geometric requirements are satisfied, x-rays scattered from a crystalline solid can be constructively interfered, consequently producing a diffracted beam. In 1912, W. L. Bragg predicted interplay relationship among several factors.⁴¹ These factors are combined and expressed in the Braggs's law: $n\lambda = 2d\sin\theta$, where: n - an interger – 1, 2, 3....., *etc.*; λ = wavelength (1.54 Å for Cu); d (d -spacing) = interatomic spacing in angstroms; θ = the diffraction angle in degrees.

What I used in my experiments is BrukerTM D8 Advanced X-Ray Diffractometer. In detail: Crystal structures of our fabricated samples were investigated by using XRD on a

BrukerTM D8 Advanced X-Ray Diffractometer with a Cu K α source ($\lambda = 0.15418$ nm).

Figure 2-3. Photo: Bruker D8 Advanced X-Ray Diffractometer. Representative XRD patterns of In₂O₃ NT samples.

§2.2.2 Raman Spectroscopy (Raman)

Raman spectroscopy is an unique and ultrasensitive spectroscopic technique and it can be used to study vibrational, rotational, and other low frequency modes in a system.⁴² As to the spontaneous Raman scattering, a photon excites the molecules from the ground states to a virtual energy states. When the molecule relaxes and then emits a photon and it proceeds to a different rotational or vibrational state. The energy difference between the original states and the new states leads to a frequency shift in the format of the emitted photons away from the original excitation energy. There are many advanced types of Raman spectroscopy techniques, including surface enhanced Raman scattering, tip enhanced Raman scattering, and polarized Raman scattering spectra, *etc.*⁴³

In my experiments, Raman spectra experiments were carried out with a WITEC CRM200 Raman system. The excitation source is 532 nm (~2.33 eV) laser, and the samples were placed on an *x-y* piezo-stage.

§2.2.3 Scanning Electron Microscope (SEM)

SEM is a microscope that utilizes electrons to generate an image. Since early 1950's, SEM has developed new areas of research in the physical/chemical science and medical communities.⁴⁴ SEM has allowed scientists to have a “close look” at a pretty big variety of specimens. Compared with normal common optical microscope, the SEM possesses much higher resolution, so closely spaced samples can be magnified at fairly high levels. Because the SEM uses electromagnets instead of lenses, the researchers have much more tunable control in the scope of magnification.

In terms of the SEM working principle, the accelerated electrons carry substantial amounts of kinetic energy, and such energy will be dissipated as a number of signals produced by electron-sample interactions at the moment that the incident electrons are decelerated on the sample. These signals include secondary electrons that produce SEM images, and photons, backscattered electrons, diffracted backscattered electrons and heat *etc.* Secondary electrons are most valuable for showing topography morphologies on samples and backscattered electrons are most appreciated for illustrating contrasts in composition in multiphase samples. SEM analysis is considered to be "non-destructive"; i.e., x-rays generated by electron interactions do not lead to volume loss of the sample, so it is conceivable to analyze the same materials repeatedly.⁴⁵

In the experiments throughout the works within my thesis, I used the Field Emission

Scanning Electron Microscopy (FESEM) branded by JEOL company (Japan), all relevant images from our samples which were acquired on JEOL JSM-6700F, operated at 10 or 15 kV.

§2.2.4 Transmission Electron Microscope (TEM)

TEM is a microscopy technique whereby a beam of electrons is transmitted through an ultrathin specimen, interacting with the specimen as it passes through. An image is generated from the interaction of the electrons and specimen; then such image is magnified and focused onto a fluorescent screen (an imaging device), or to be detected by a camera such as a CCD.⁴⁶

Diffraction contrast is a dominant mechanism for imaging and investigating the dislocations and defects in a specimen. The effect of the crystal potential will modify the phase of the incident electron wave. The variation of the projected crystal potential leads to the change of electron phase. The contrast produced by such mechanism is called phase contrast.

In my experiments, the structural properties and micro-structures with dislocations and/or defects of related samples were investigated by using a high resolution transmission electron microscopy (HRTEM, JEOL 2100F) at an accelerating voltage of 200 kV.

§2.2.5 Energy-Dispersive X-ray Spectroscopy (EDS)

EDS works via detecting x-rays that are produced by a sample placed in an electron

beam. The electron beam excites the atoms in the specimen that subsequently produce x-rays to release the excess energy. Owing to the electron beam can be precisely controlled; EDS spectra can be obtained on a specific point from the sample, providing an analysis of a few cubic microns volume of material. Alternatively, the beam can also sweep over a desired area of the sample to identify the elements in that region. Moreover, the line profiles and x-ray maps can be acquired which illustrate the elemental distribution across the specimen. Phases or features as small as $\sim 1 \mu\text{m}$ or less is able to be analyzed.⁴⁷

The equipment is attached to the SEM or TEM to allow for elemental analysis information to be collected about the specimen under investigation. The technique is non-destructive and has a sensitivity of $>0.1\%$ for elements heavier than C.^{48, 49}

§2.2.6 X-ray Photoelectron Spectroscopy (XPS)

XPS is a quantitative spectroscopic technique that probes the surface chemical composition, empirical formula, valence states and electronic states of the elements that exist within a specimen. XPS spectra are acquired by irradiating a specimen with an x-rays beam which carries certain energy while simultaneously measuring the kinetic energy and number of electrons that escape from the surface (1 to 10 nm) of the specimen being analyzed. XPS requires ultra high vacuum condition.⁵⁰

In terms of the basic working principle: because the energy of a particular x-ray wavelength is known, the electron binding energy of each of the emitted electrons can be obtained by using an equation that is based on the work of Ernest Rutherford:

$$E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi)$$

where E_{binding} is the binding energy of the electron, E_{photon} is the energy of the x-ray photons being used, E_{kinetic} is the kinetic energy of the electron as measured by the instrument and ϕ is the work function of the spectrometer.

XPS is a surface chemical analysis technique that can be used to analyze the surface chemistry of a material in its "as received" state, or after some specific treatments. XPS detects all elements with an atomic number (Z) of 3 (Li) and above. Detection limits for most of the elements are in the parts per thousand range. Detection limits of parts per million (ppm) are possible, but require special conditions: concentration at top surface or very long collection time (overnight).⁵¹

XPS is routinely utilized to analyze:

1. Elemental composition of the surface and chemical or electronic states of each element;
2. Elements that contaminate a surface;
3. Uniformity of elemental composition across the surface;
4. Uniformity of elemental composition with a depth profiling;
5. Empirical formula of materials.

§2.2.7 Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

SIMS is a technique used in materials surface science. By sputtering the surface of the specimen with a focused primary ion beam and collecting and analyzing ejected secondary ions, we can analyze the composition of solid and thin films. These secondary ions are measured with a mass spectrometer to determine the elemental, isotopic, or molecular composition of the surface. SIMS is supposed to be the most sensitive surface

analysis technique, and being able to detect elements present in the parts per billion range.^{52, 53}

ToF-SIMS utilizes a focused, pulsed particle beam (typically Cs or Ga) to dislodge chemical species on a materials surface. Owing to its capability of measuring the "time-of-flight" of the particles on a scale of nano-seconds, it is able to produce a mass resolution as fine as one part in a thousand of the mass of a proton.

If there were organic contaminants adsorbed on the surface, such as oils, ToF-SIMS would disclose such information, whereas other techniques might not. Since ToF-SIMS is a survey technique, all the elements in the periodic table, including H, are detected. Moreover, ToF-SIMS can provide the image information in the XY dimension across a specimen; and also depth profile information on the Z dimension into a specimen. Should you know what you are going to deal with, then you can use other techniques to obtain additional complementary information.

In my experiments, the materials surface properties, i.e., elemental composition of relevant samples were investigated with a TOFSIMS IV instrument from IONTOF GmbH. <http://www.ion-tof.com/>. It possesses a high mass resolution above 7000, high sensitivity and unlimited mass range.

§2.2.8 Atomic Force Microscope/Magnetic Force Microscope (AFM/MFM)

AFM is one kind of scanning probe microscopes, which is designed to investigate the local properties of a material, such as height, friction and magnetism *etc.* with a

specific tip probe. In order to obtain an image, by adopting different functional scanning tips under certain environment, the extended AFM scanning modes probe a defined area of the sample, testing the local properties simultaneously.⁵⁴

AFM operates by examining the force between the probe and the sample. Generally, the probe is a sharp tip, which has a 2-6 μm height pyramid structure with 2-40 nm end radius. The lateral resolution of AFM scanning is around 20 nm due to the convolution due to the coupling shape effect from tip itself; however, the vertical scanning resolution can be down to <0.1 nm. To acquire the image resolution, AFM can normally measure the vertical and lateral deflections of the cantilever by using the optical lever. The optical lever works via reflecting a laser beam off the cantilever. The reflected laser beam strikes a position-sensitive photo-detector consisting of four-segment photo-detector. The differences between the segments of photo-detector of signals indicate the position of the laser spot on the detector and thus the angular deflections of the cantilever (**Figure 2-4**).

Figure 2-4. Working status of an AFM with an optical lever.

A well-constructed feedback loop is essential to microscope performance (**Figure 2-5**). The feedback loop consists of the tube scanner that controls the height of the tip; the cantilever and optical lever, which probes the local height of the sample, and a feedback

circuit that tends to keep the cantilever deflection constant by adjusting the voltage applied onto the scanner. There are many fabulous scanning modes developed from conventional AFM functionalities, for example, scanning Kelvin probe microscope, peizo-responses force microscope, electrostatic force microscope, magnetic force microscope (MFM) *etc.* MFM is a variation of AFM,⁵⁵ where a sharp magnetized tip coated with a layer of magnetic material is scanning the sample, the tip-sample magnetic coupling interaction (i.e., magnetic dipole–dipole interaction) is to be detected and used to reconstruct the magnetic domain structure of the sample surface.

Figure 2-5. AFM feedback loop diagram and an AFM image of ZnO nanobelts with $6\ \mu\text{m} \times 6\ \mu\text{m}$ scanning area.

MFM often works under a non-contact AFM (NC-AFM) scanning mode. During MFM measurements, the formed magnetic force between the sample and the tip can be expressed as $\vec{F} = \mu_0 (\vec{m} \bullet \nabla) \vec{H}$, where $\vec{m}$ is the magnetic moment of the tip, $\vec{H}$ is the magnetic stray field from the sample surface, and μ_0 is the magnetic permeability of free space. Typical resolution of $\sim 30\ \text{nm}$ can be achieved,⁵⁶ although resolutions as low as 10 to 20 nm are attainable.

In my experiments, AFM/MFM images and height profiles were taken on a scanning probe microscope (Veeco Digital Instruments) with Si and Si coated with Co magnetic layer probe tips.

§2.2.9 Photoluminescence (PL)

PL spectroscopy is a nondestructive method of measuring the electronic structure of materials. It is a physical process in which a substance absorbs photons and then reradiates photons. Quantum mechanically speaking, this can be described as a photo-excitation to a higher energy state and then a relaxation to a lower energy state accompanied by the emission of photons. One way such excess energy can be dissipated by the sample is the emission of light, which is luminescence, called photoluminescence.

The intensity and spectral feature of such photoluminescence is a direct measure of various important properties of a material.⁵⁷ A fundamental understanding can be attained by studying the molecular orbitals and electron configurations of simple atoms and molecules.⁵⁸ The most common radiative transition in semiconductors is between states in the conduction and valence bands, with the energy difference being known as the “band gap”. Radiative transitions in semiconductors normally also involve localized defect levels. The amount of PL and its dependence on the level of photo-excitation and temperature are directly related to the dominant recombination process. Analysis of PL helps to understand the underlying physics of the recombination mechanism.

§2.2.10 Time-Resolved Photoluminescence (TRPL)

TRPL setup explores how the luminescence emitted by optically-excited samples varies with time, where the time period can be on the order of nano or picoseconds. Analysis of the ultrafast behavior of light emitted from samples can reveal vital information about the recombination processes involved, including the lifetimes of the various transitions.^{59, 60} Our setup includes:

- Coherent Legend, regenerative amplifier system pumping an optical parameter amplifier – Light conversion TOPAS
- Hamamatsu C5680 Series Universal Streak Camera – for temporal and spatial analysis of the light pulse; dual-stage Liquid Helium Cryostat – for cooling samples down to ~4.2 K
- PicoQuant Picosecond Laser system – alternative excitation source

Main features:

- 2 picoseconds temporal resolution
- High excitation power density ~15 kW/cm²
- Temperature range: 4.2 ~ 350 K
- Simultaneous measurement of light intensity on temporal and spatial axes - time-resolved spectroscopy
- Ultra-high sensitivity - single photon detection

§2.2.11 Superconducting Quantum Interference Device (SQUID)

SQUID is a very sensitive magnetometer used to measure extremely weak magnetic fields, based on superconducting loops comprising the Josephson junctions.⁶¹ SQUID is

sensitive enough to measure fields as low as 5 atto tesla of averaged measurements within a few days. The noise levels are on the order of $3 \text{ fT} \cdot \text{Hz}^{-1/2}$.⁶² For comparison, a typical refrigerator magnet produces 0.01 tesla (T), and some processes in animals usually produce very small magnetic fields in the range of $10^{-9} \sim 10^{-6} \text{ T}$. There are mainly two types of SQUID: direct current (DC) and radio frequency (RF). RF SQUIDs can work with only one Josephson junction, which might make them cheaper to produce, but with less sensitivity.

Figure 2-6. Photo: MPMS made by Quantum Design with SQUID inner structure.

Representative *M-H* loops of Cu-doped ZnO NW samples.

The most common use of SQUIDs is in magnetic property measurement systems (MPMS). Developed by Quantum Design company, MPMS MultiVu software built in system probes the magnetic moment of a sample by reading the output of the SQUID detector while the sample moves upward, from the initialization position, through the SQUID pickup coils. At each position in the coils, the magnetic moment calibration for the MPMS is determined by measuring a Pd reference over a range of magnetic fields and then by adjusting the system calibration factors to obtain the correct magnetic moment for the reference. The reference is a right circular cylinder approximately 3 mm in diameter and 3 mm in height. Owing to the geometry of the SQUID pickup coils, samples of this size or smaller are effectively point sources to an accuracy of approximately 0.1%.

In my experimental implementations, magnetization measurements were carried out by using a superconducting quantum interference devices magnetometer (SQUID, Quantum Design, MPMSXL-5). Throughout the synthesis and measurement steps, only plastic tweezers were utilized to avoid any potential contamination from metal tools.

Chapter 3 Mechanism and Physical Origin of Ferromagnetism in Undoped ZnO Nanowires

§3.1 Correlated d^0 Photoluminescence and Ferromagnetism in Undoped ZnO Nanowires

§3.1.1 Overview

Recently, RTFM has been reported in ZnO doped with TMs such as Mn, Co and Cu, which makes ZnO promising for spintronics applications.³⁻⁵ However, besides the issues of stability and reproducibility, it remains controversial whether RTFM is intrinsic or due to extrinsic origins such as metal clusters and precipitates of impurity phases. Adding to these existing literatures, there have been a few notable reports on RTFM in undoped ZnO. So far, most of the previous magnetic studies on pure ZnO have concentrated on bulk and thin film samples. To the best of our knowledge, there has been no systematic investigation on the magnetic characteristics of undoped ZnO NWs. With high surface-to-volume ratios, the electronic configuration of one-dimensional NWs is amenable to be altered, which could be used as a tool to establish long range magnetic ordering.⁹

In this section, we report a comparative study on the FM in undoped single-crystalline ZnO NWs grown by the vapor transport method. By carefully selecting the catalyst and varying the growth temperature, we can reproducibly tune the oxygen content in the NWs, which is accompanied by the characteristic defect-related emissions in the PL spectra. Our systematic studies suggest that both the photoluminescence and the

RTFM are closely correlated with the oxygen deficiency in the undoped ZnO NWs.

§3.1.2 Experimental details

Three types of ZnO NWs were prepared by using the vapor transport method in a horizontal tube furnace (Lindberg/Blue Mini-Mite) equipped with a gas supply and pumping system. The experimental setup was described in earlier **Chapter 2**. Typically, ZnO or Zn powder was used as the source, and argon mixed with 5% oxygen was used as the carrier gas. Silicon substrates were sputtered with 2 nm Au or Ag film as the catalyst. The experimental conditions and the properties of the synthesized NWs are summarized in **Table 3-1**.

Table 3-1. Growth conditions and experimental results of undoped ZnO NWs grown by the vapor transport method.

Sample	Source	Catalyst	Source temperature	Substrate temperature	Oxygen deficiency (%)	GB/UV emission ratio	H_c at 5 K/RT (Oe)	M_s at RT (μ_B/V_O)
NW1	ZnO/C	Au	960 °C	850 °C	20	62.58	190/115	0.0076
NW2	Zn	Au	520 °C	470 °C	10	2.87	145/76	0.0030
NW3	Zn	Ag	520 °C	470 °C	4	0.04	77/44	0.0003

§3.1.3 Morphology and structural properties

SEM, XRD and TEM results

We systematically adjusted the synthesis conditions and selected three kinds of typical samples to illustrate the interesting structure-property correlation. As shown in the SEM images in **Figure 3-1** (a), Au catalyst and a high growth temperature (960 °C) give randomly dispersed NWs (sample NW1) with diameters of 50-100 nm and lengths of a

few micrometers, wherein the VLS growth mechanism dominates the growth process. On the other hand, a low temperature (520 °C) growth gives thicker and shorter NWs [Figure 3-1 (b), sample NW2], because Au nanoparticles merely serve as nucleation sites, trapping Zn vapor. Thus the NW2 sample growth catalyzed by Au is governed by VS growth mechanism. Interestingly, we found the Ag catalyzed sample grown at the low temperature (sample NW3) yields vertically aligned NWs [Figure 3-1 (c)] on substrate with smaller diameter and length; this should be resulted from the squeezing between the nanowires each other, because compared with Au, nano-size Ag catalyst possesses a lower melting point, the smaller diameter of Ag particles will be formed with the higher density at low temperature.

Figure 3-1. SEM images of ZnO NWs in (a) NW1, (b) NW2, and (c) NW3. The scale bars: 1 μm . (d) Corresponding XRD patterns. (e) XPS survey scan of NW1, inset shows the XPS O 1s detailed scan.

In the XRD patterns [**Figure 3-1** (d)], all peaks can be identified with the crystalline wurtzite ZnO structure. Except the catalyst Au in NW1 and NW2, there is no detectable secondary impurity or phase. Transmission electron microscopy experiments were also carried out to investigate the sample structures; extensive observations suggest that all three kinds of NWs possess high crystalline quality with no structure defects detected.

§3.1.4 Chemical compositions and valence states

XPS results and comparison

XPS measurements were performed on these NW samples to assess the oxygen content. The sample surface was cleaned by argon ions with an etching rate of 3 nm/min. As the penetration depth of Al $K\alpha$ XPS is several nm, after the samples were peeled off, the compositions determined for the NWs should be close to the actual values, which permitted quantitative comparisons among the samples. The survey scans show no impurity above the detection limit.

Figure 3-2 (a)-(c) depict the multi-component fitting to the O 1s peaks in NW1, NW2 and NW3, respectively, which were normalized by the Zn 2p peaks accordingly. The peaks at lower and higher energies can be attributed to O^{2-} ions and absorbed oxygen, respectively.¹¹ The chemical compositions were determined by applying the calibrated atomic sensitivity factors and fitting to the integrated intensities of the XPS core-level peaks. We determined the nonstoichiometric formula for samples NW1, NW2 and NW3 to be $ZnO_{0.80}$, $ZnO_{0.90}$, and $ZnO_{0.96}$, respectively, and the corresponding O/Zn atomic ratios were plotted in **Figure 3-2** (d). Previous theoretical predictions have suggested that

the high oxygen deficiency in oxides should be attributed to oxygen vacancies rather than cation interstitials due to their lower formation energy.¹² Thus we can conclude that the concentrations of oxygen vacancies were systematically adjusted in these samples. Moreover, NW2 and NW3 were grown under very similar condition except the different catalysts used. The different oxygen content appears in NW2 and NW3 with employment of different catalyst, which could be due to that: Ag has the highest electrical conductivity and the highest thermal conductivity among all metals, therefore the absorbed surface atoms or molecules are equipped with high mobility and are distributed uniformly, occupying the energetically favorable sites during growth, to form NWs structure efficiently than those NWs catalyzed by Au. Eventually Ag catalyzed NWs, i.e., NW3 growth process undergoes shorter formation duration in the oxygen-poor environment. Hence, Ag-catalyzed NW3 contains relatively higher oxygen content.

Figure 3-2. (a-c) Normalized XPS O1s core-level peaks. (d) O/Zn atomic ratios of three types of NWs.

Optical properties characterization

Figure 3-3. (a) RT PL spectra of NW1, NW2, and NW3. (b) 5 K PL spectra of NW1 and NW3. (c) Enlarged view of the NBE region of NW1 and NW3 at 5 K. (d) Temperature dependent PL spectra of NW1 in the temperature range from 5 to 300 K.

PL measurements were performed by using a He-Cd laser with an excitation wavelength of 325 nm. In the PL spectra taken at RT [Figure 3-3 (a)], a near-band-edge (NBE) UV peak dominates in NW3, but significantly weaker in NW1. On the other hand, NW1 is featured with a broad deep level emission (DLE) in the visible region, which can be ascribed to the transitions of the excited optical centers from the deep levels to the valence band.¹³ These deep levels are associated with the intrinsic defects in the NWs,

presumably oxygen vacancies. The integrated intensity ratio of the defect green emission to the UV emission (GB/UV) is largest in NW1 and smallest in NW3. Considering this strong contrast, we focus on the PL results obtained on these two samples.

Figure 3-3 (b) illustrates the low temperature (5 K) PL spectra for NW1 and NW3. The NBE emission dominates the PL spectra of NW3, and as shown in **Figure 3-3** (c), the associated fine structures were clearly resolved. The emission peaks at 3.365 and 3.360 eV can be identified to excitons bound to neutral donors (D^0X)^{2, 13} and acceptor-bound excitons (A^0X)² respectively. In **Figure 3-3** (b) the peak located at 3.310 eV might be the first LO photon replica of the free exciton ($1LO-FE_A^{n=1}$).² The D^0X NBE emission is much stronger in NW1 than that in NW3 due to the presence of high-density oxygen vacancies as donors. In **Figure 3-3** (b), DLE (green emission band) shows fine structures, which repeat with a longitudinal-optical-phonon-energy spacing (~ 72 meV) and are associated with the transitions involving shallow donors (oxygen vacancies).¹⁴ **Figure 3-3** (d) shows the temperature- dependent PL spectra of NW1, illustrating the evolution of the dominant DLE from RT down to 5 K.

The intriguing experimental results of distinct oxygen contents in ZnO NWs by utilizing different catalyst of Au and Ag warrant the further studies to investigate more insight into the critical role of catalyst, and also motivate people to perform growth of NWs similar to NW3 but with reduced oxygen and see if it can generate peaks in PL for the NWs.

§3.1.5 Magnetic characteristics: SQUID results and discussions

Figure 3-4. (a) M - H loops of NW1, NW2 and NW3 taken at 5 and 300 K. (b) ZFC and FC temperature-dependent magnetization curves.

The contrasts in oxygen content and optical characteristics in samples NW1, NW2 and NW3 motivated us to conduct a comparative study on their magnetic properties. Magnetization measurements were carried out by using a SQUID. Only plastic tweezers were used throughout the experiments to avoid any unintentional metal contamination. The Si substrates diamagnetic backgrounds were deducted from the raw data. Considering that nanoscale Au, Ag may induce weak FM,^{15, 16} we first investigated the magnetic properties of the Si substrates coated with Au or Ag thin films. All substrates without NWs growth showed only diamagnetic behaviors. **Figure 3-4** (a) depicts the magnetization versus magnetic field (M - H) curves measured on NW1, NW2 and NW3 at 5 and 300 K. Both NW1 and NW2 exhibit clear hysteresis loops, suggesting RTFM. In contrast, the magnetism is very weak in NW3. Remarkably, the magnetization of NW1 is almost 25 times higher than that of NW3. As can be seen in **Figure 3-4** (b), the magnetizations *vs.* temperature (M - T) curves were measured with both zero-field-cooled (ZFC) and field-cooled (FC) conditions under a magnetic field of 500 Oe. Consistent with the M - H data, the temperature-dependent magnetization of NW1 is much stronger than

those of NW2 and NW3, which ascribe to the presence of substantial oxygen vacancies in NW1.

Figure 3-5. RT saturation magnetizations and GB/UV emission ratios of NW1, NW2 and NW3 vs. the corresponding oxygen deficiency levels.

§3.1.6 Discussions on RTFM mechanisms

A comparative study on these three kinds of NW samples disclosed a strong correlation between the oxygen deficiency and the FM. The RT saturation magnetizations and the GB/UV emission ratios of NW1, NW2 and NW3 vs. their corresponding concentrations of oxygen deficiency are shown in **Figure 3-5**. The trend is clear: oxygen vacancies boost both the GB emission and the magnetism. However, it is noteworthy that the GB/UV emission ratio in NW1 is more than 20 times higher than that in NW2 while changes in the oxygen deficiency level and saturation magnetization are much more modest. This result indicates that a certain density of oxygen vacancies is needed in order to completely quench the NBE emission. Although both PL and magnetic properties are

closely linked with the oxygen deficiency, the associated physical mechanisms and their quantitative dependence are very different.

The composition of the samples has been checked with a time interval on purpose. We performed the composition analysis using x-ray photoemission spectroscopy, but we need to be prudent as the signal is slight different for different sample in the same batch, but the trend of doping is quite clear. The change in oxygen concentration can result in a modification of the sample's magnetic properties, but in our experiments, the same samples were measured by SQUID two times before and after XPS probing within a week, so the comparison in **Figure 3-5** is still valid.

RTFM has been observed previously in undoped wide-band-gap oxide thin films and nanoparticles such as TiO_2 , HfO_2 , In_2O_3 , CeO_2 and SnO_2 , and its origin is usually linked to the oxygen deficiency.^{17, 18} These findings of RTFM with the absence of any transition metal doping have attracted significant attention and were called ' d^0 FM'.¹⁹ The RTFM in our samples can be attributed to the large population of bond defects, i.e., V_o , since they can initiate defect-related hybridization at the Fermi level and establish a long-range ferromagnetic ordering.²⁰ A high concentration of V_o could also promote the probable formation of anionic vacancy clusters which can induce sizable magnetic moments.⁶ Although our result does not exclude other types of defects like cation vacancies as the origin of long range ferromagnetic ordering,^{21, 22} these defects often have higher formation energy than V_o and can form only in oxygen rich environments.²³ Our experiments were carried out in oxygen poor conditions where V_o always contributes to the nonstoichiometry.²⁴ The tunable RTFM in NW samples confirms that oxygen vacancies can be purposely used to establish and regulate the ferromagnetic ordering.

§3.1.7 Summary

In summary, undoped ZnO NWs with diverse and reproducible optical and magnetic properties were synthesized via a facile vapor transport method. We found that the concentration of oxygen vacancies directly regulates both the well-known defects-related green emission and the FM. The present study not only demonstrates that undoped ZnO NWs can emit green light and show RTFM with energetic stability, but also suggests that introducing oxygen vacancies is an effective way to boost the d^0 FM. These engineered NWs with carefully tailored composition may find potential applications in nanoscale spintronic devices.

§3.2 Interface Induced Ferromagnetism in Core/Shell Structured ZnO Nanowires

§3.2.1 Introduction

Recently, RTFM has been reported in ZnO doped with transition metals, which makes ZnO promising for spintronics applications.^{21, 63, 64} However, the issues of stability and reproducibility make debates exposed upon that RTFM is intrinsic or due to metal clusters and precipitates of impurity phases. Recently, there have been a few reports on RTFM in undoped ZnO, most of the reports linked observed RTFM to the formation of intrinsic defects or domain boundaries. Besides, C. N. R. Rao and co-workers have suggested that the surface-confined universal FM observed in most inorganic nanoparticles could be used in many interesting ways.⁶⁵ Most recently, Y. W. Ma *et al.*

claimed that the FM observed in heterostructured ZnO–Al₂O₃ thin film may be attributed to the microstructure of ZnO nanocrystals embedded in alumina-based ZnO–Al₂O₃ amorphous matrix.⁶⁵ As Dr. Ogale pointed out in a recent review,⁶⁶ the defect-related considerations have led to the reemergence of the field of defect FM. In contrast, the case of interface FM is of great interest because the corresponding state of the material can be growth controlled and stabilized.

With high surface-to-volume ratios, the electronic configuration of one-dimensional NWs is amenable to be altered, which could be used to establish long range magnetic ordering.⁶⁷ In this section, I present a comparative study on the FM in composited ZnO NWs grown by a vapor transport method followed by an atomic layer deposition technique and the thermal annealing treatment. By carefully varying the preparation conditions, we can reproducibly tune the interface coverage in core/shell structured ZnO NWs, which are accompanied by the characteristic defect-related ferromagnetic signals in the *M–H* plots. Our systematic studies suggest that the observed RTFM in composited ZnO NWs is closely correlated with the interface defects which can be modulated by surface modification of undoped ZnO NWs.

§3.2.2 Experimental details

Single-crystal ZnO NWs were prepared in a horizontal tube furnace by means of vapor transport deposition method. The experimental setup was described in earlier **Chapter 2**. Si substrates were sputtered with 2 nm Au film as the catalyst. The ZnO-based core/shell structured NWs were synthesized by using an atomic layer deposition method and a delicate post-annealing treatment, respectively.

§3.2.3 Physical properties of ZnO-based NWs: comparative investigation

Figure 3-6. SEM images of (a) uncoated ZnO NWs (UZO), (b) Al_2O_3 coated ZnO/ Al_2O_3 (AZO) and (c) ZnO/ ZnAl_2O_4 (A-AZO) core/shell structured NWs. The scale bars are 300 nm. (d) and (e) Corresponding XRD patterns.

We systematically adjusted the synthesis conditions and selected three typical samples to illustrate the interesting structure-property correlation. As shown in **Figure 3-6** (a), as-grown uncoated ZnO NWs (UZO) were grown on Si substrate with diameters of 50-100 nm and lengths of $\sim 2 \mu\text{m}$. On the other hand, 15 nm thick Al_2O_3 layer coated ZnO NWs appear with thicker diameter and smoother surface [**Figure 3-6** (b), sample AZO]. We further annealed the core/shell NWs in air at 800 $^\circ\text{C}$ for 3 h. Interestingly, we found the annealed ZnO/ Al_2O_3 core/shell NWs (sample A-AZO) show very rough surface [inset

of **Figure 3-6 (c)**] in comparison with other two kinds of NWs. In the XRD patterns [**Figure 3-6 (d)**], all peaks can be identified with the crystalline wurtzite ZnO structure. There is no detectable secondary impurity or phase even though the amorphous Al_2O_3 coated layer on ZnO NWs. The dominant (002) ZnO peak in all samples corroborates the preferred growth orientation, which is consistent with previous reports.^{3, 68} Clearly, the ternary compound of ZnAl_2O_4 phase emerged in the dominated ZnO diffraction peaks [**Figure 3-6 (e)**].

Figure 3-7. *M-H* data taken on the Si substrates coated with 2 nm Au showing the diamagnetic behaviors.

The contrast in morphologies and structural characteristics among samples of UZO, AZO and A-AZO motivated us to carry out a comparative study on their magnetic properties. Magnetization measurements were performed by using a superconducting quantum interference devices magnetometer. Only plastic tweezers were used throughout all the experimental steps to avoid unintentional metal contamination. The diamagnetic

backgrounds of the Si substrates coated with 2 nm Au were subtracted from the raw data (Figure 3-7). Furthermore, considering that the nanoscale ZnAl_2O_4 may induce weak ferromagnetic signals, we first investigated the magnetic characteristics of the sintered ZnAl_2O_4 nanocrystals and found that they actually exhibit an obvious diamagnetic behavior.

Figure 3-8. (a) M - H loops of UZO, AZO and A-AZO NWs taken at 5 and 300 K. (b) Raw data without the subtraction of the substrate signal measured on sample of A-AZO, in comparison with diamagnetic substrate. (c) RT M - H data of UZO and AZO samples with various Al_2O_3 coating thickness: 5, 15 and 30 nm. (d) M - T curve of the A-AZO sample in the extended temperature range of 5-780 K. Inset shows ZFC and FC

temperature dependent magnetization curves of sample A-AZO and AZO measured from 5 K to 380 K.

Representative substrate without NWs growth showed only diamagnetic behaviors [Figure 3-8 (b)]. Figure 3-8 (a) depicts the $M-H$ curves measured on UZO, AZO and A-AZO at 5 and 300 K, respectively. Both AZO and A-AZO exhibit clear hysteresis loops, suggesting RTFM. In contrast, the magnetism is very weak in UZO. Remarkably, the magnetization of A-AZO is about 45 times higher than that of UZO. It is not surprising that the observed ferromagnetic signals should attribute to interface induced defects amount but not resulted from the coated Al_2O_3 layer, since there is no shell thickness dependence on magnetization as demonstrated in Figure 3-8 (c). Moreover, we have studied several samples with different sizes which had been broken from the same parent sample, it shows out that the magnetic properties are quite similar, suggests negligible contamination. Thus the magnetic comparison among the UZO, AZO and A-AZO samples is valid.

As shown in the inset of Figure 3-8 (d), the magnetizations versus temperature curves were measured under a magnetic field of 500 Oe under both zero-field-cooled and field-cooled conditions. In accordance with the $M-H$ data, the temperature-dependent magnetization of A-AZO is much stronger than of AZO, which is ascribed to the presence of substantial interface defects in A-AZO. High-temperature $M-T$ experiments were also carried out in our SQUID with oven, as shown in Figure 3-8 (d), which reveals a magnetic behavior with a magnetic signal persisting up to ~673 K.

Figure 3-9. TEM results of individual NW of (a) UZO, (b) AZO and (c) A-AZO. Insets show the corresponding SAED patterns and HRTEM images. (d) shows the enlarged HRTEM image of A-AZO NW.

Transmission electron microscopy experiments were further carried out on samples to investigate the structural properties; extensive observations suggest that UZO NWs exhibit single-crystal structure with free cluster and secondary phase. The growth direction was determined to be along with [001] orientation which is in agreement with the selected area electron diffraction (SAED) pattern. While after ALD deposition of an alumina layer on sample UAO, as shown in **Figure 3-9** (b), ZnO/Al₂O₃ core/shell NWs were obtained. The alumina coating does not change the morphology and growth direction of ZnO NW. The amorphous alumina layer with around 15 nm thickness can be

clearly observed and there is no void or gap was formed, which is different from previous reports.^{69, 70}

Figure 3-10. TEM image and EDS spectrum of sample AZO. (a) TEM image of an individual AZO NW with elements line scanning curves. (b), (c) and (d) show the corresponding elemental mappings.

The local composition of the core/shell NWs was investigated with energy-dispersive x-ray spectra by line scanning across the NW axis, **Figure 3-10** (a). The intensity profile of Zn and Al reveals a typical coaxial ZnO core/Al₂O₃ shell NW structure. ALD deposition is a sequential and self-limiting process. Its layer-by-layer growth mode ensures a precisely controlled, pinhole-free and conformal Al₂O₃ film is deposited around the ZnO NW. Unexpectedly, after annealing treatment in air at 800 °C for 3 h, the stimulated solid-state reaction occurred surrounding the interface regions between the core of ZnO and the shell of alumina layer. Consequently, after extensive probing by

means of high-resolution TEM (HRTEM), the ternary compound of ZnAl_2O_4 was observed as the adhesive coating shell and resulting in much rough surface on ZnO core NWs. Spontaneously, as shown in **Figure 3-9** (d), there appear much disordered structures (D. S.) such as, stacking faults (S. F.) on the boundaries of sample A-AZO, which were highlighted by polygon curves (for more details of observed disordered structures in sample of A-AZO, see **Figure 3-11**). Crystalline spinel ZnAl_2O_4 through interface solid state reaction of $\text{ZnO}/\text{Al}_2\text{O}_3$ core/shell nanowires occurred involving the Kirkendall-type diffusion. Such core/shell structured $\text{ZnO}/\text{ZnAl}_2\text{O}_4$ NWs were obtained by forming the core/shell structure $\text{ZnO}/\text{Al}_2\text{O}_3$ NWs and following a delicate post-annealing treatment. Unlike the previous report of hollow ZnAl_2O_4 nanotube synthesis induced by Kirkendall effect [Fan *et al.*, *Nature Materials* 5, 627, (2006)], in our experiment, the combination of well-designed core/shell $\text{ZnO}/\text{Al}_2\text{O}_3$ with particular thickness (15 nm) and a controlled post-annealing (800 °C for 3 h in air) plays a critical role for the formation of final core/shell structured $\text{ZnO}/\text{ZnAl}_2\text{O}_4$ NWs, instead of ZnAl_2O_4 nanotube.

Based on above extensive TEM observations, we can come to the conclusion that the sample A-AZO possesses much more rough surfaces in comparison with sample of AZO even though they have the same core/shell NWs structure. EDS experiments were also carried out to investigate the A-AZO sample structures, extensive observations suggest that core/shell structured NWs with inhomogeneous elements distribution (**Figure 3-12**).

Figure 3-11. HRTEM image of individual NW of sample A-AZO. Right side shows the corresponding SAED patterns.

Our comparative structure-property study on these three kinds of composited NW samples revealed a strong correlation between the FM and the interface defects. The trend is quite clear: the FM is enhanced by the interface defects even though undoped ZnO NWs were decorated by different materials, like amorphous alumina and ternary ZnAl_2O_4 compound. RTFM has been observed previously in undoped wide-band-gap oxide thin films and nanoparticles such as TiO_2 , HfO_2 , In_2O_3 and CeO_2 ,⁷¹⁻⁷³ and its origin was usually linked to the oxygen deficiency.^{65, 74, 75} The formation of the magnetic moment was tentatively attributed to holes localized at cation vacancies even in large band gap nonmagnetic CaO .⁷⁶ These findings of RTFM with the absence of any transition metal doping have attracted significant attention and were called ' d^0 FM'.⁷⁷ There have been reports suggesting that unpaired electrons can induce magnetism. Based on the theoretical simulation using density function theory, Schoenhalz *et al.*⁷⁸ reported that the magnetic moment highly depends on the ZnO NC size. C. N. R. Rao and co-workers^{65, 79} suggested

that the origin of FM is due to the unpaired electron spins which have origin in the oxygen vacancies on the surfaces of ZnO NCs. These electrons located at the oxygen vacancies are polarized and can induce FM. With this frame work, the FM found in our samples may be due to the interface defects of ZnO core/shell structured NWs.

Figure 3-12. Extensive TEM images and EDS spectrum of sample A-AZO (a) TEM image of an individual A-AZO NW. (b), (c) and (d) show the corresponding elemental mappings. (e) EDS spectrum of sample A-AZO. (f) TEM image of an individual A-AZO NW with line elements scanning curves (g).

The origin of FM in ZnO has been also previously studied using first-principle methods and was attributed to the localized nature of the $2p$ states of O.⁸⁰ In other words, it is caused by the strong spin-exchange interaction at the O sites due to the large density of states in the ionic oxides near the valence band maximum.⁸¹ Indeed our experimental results suggest that the magnetic behavior of the core ZnO NWs is dictated by the

concentration of interface defects which resulted from purposely adhered to shell layers of Al_2O_3 or ZnAl_2O_4 . A substantial amount of interface defects could promote the probable formation of anionic vacancy, i.e., oxygen vacancies (V_o) clusters which can induce sizable magnetic moments.⁷⁴ The spin-split impurity band theory,⁸¹ which suggests that the shallow donor concentration must be high enough to trigger the paramagnetism-FM transition. Such intriguing experimental results of distinct FM in core/shell in ZnO NWs by adjusting interfaces warrant the further studies to get more insight into important role of interface, and also motivate people to perform comparative studies to investigate the post-annealing treatments in diverse ambient see if it can generate the same tunable magnetization properties in such core/shell structured NWs.

§3.2.4 Summary

In summary, undoped ZnO NWs with diverse and reproducible structural and magnetic properties were synthesized by a facile vapor transport method, atomic layer deposition method and thermal annealing treatment as well. The surface and interface in these NWs were systematically adjusted, which were strongly correlated with the SQUID data. Most importantly, we found that the coverage of interfaces on ZnO core NWs directly regulates the FM. The interface defects engineering is of great interest because the corresponding state of the material can be growth controlled and stabilized. The present study suggests that introducing interface defects is an effective way to boost the d^0 FM, and the composition engineered NWs may find potential applications in nanoscale spintronic devices.

Chapter 4 Structure, Ferromagnetism Origin and Spin Polarization Studies in Cu-ZnO Nanowires

§4.1 Comparative Study of Enhanced Room Temperature Ferromagnetism in Cu-ZnO Nanowires by Structural Inhomogeneity

§4.1.1 Introduction to Cu-doped ZnO

Since 1982, studied as a synthesis catalyst for methanol,⁸² Cu-doped ZnO stimulated lots of interests most recently because that the Cu-based compounds are non-ferromagnetic and Cu atoms have no clustering tendency in DMS research community.⁸³ Thus, Cu doping strategy overcomes the issues of magnetic precipitates formation in DMS. Indeed, several theoretical computations predicted that Cu-doped ZnO has a ferromagnetic ordering even at room temperature.⁸⁴⁻⁸⁶ These theoretical calculations were later on verified by experimental observations of RTFM in ZnO thin films doped with Cu. However, Keavney *et al.* didn't ascertain any significant spin polarization from Cu 3*d* and O 2*p* states in Cu-doped ZnO via magnetic circular dichroism studies although the thin film samples exhibited RTFM without any contamination as claimed.⁸⁷ Such interesting results imply that the physical origin of RTFM in Cu-doped ZnO is not clear and different from the carrier-mediated mechanism, therefore it warrants further investigations.

In this section, I'm going to report a comparative study for RTFM in ZnO NWs doped with Cu synthesized by 2 distinct schemes. Compared with the previous reports

adopting the single approach of sample fabrications, such systematic study helps to eliminate the unintentional experimental artefacts and to manifest the origin and mechanism of observed phenomena in DMS. Here, I present a mechanism that the structural inhomogeneity could significantly boost the FM in Cu-doped ZnO NWs DMS system.²¹

§4.1.2 Experimental details

The ZnO NWs and Cu doped counterparts were synthesized using vapor phase transport method.

For the 1st synthesis scheme, the mixed ZnO and CuO (99.99%, Aldrich) powders were ground for 0.5 h, cold pressed and calcined at ~500 °C for 16 hours. Such grinding and pressing procedure was repeated and another sintering was conducted for 12 hours at ~800 °C to obtain homogeneously doped ZnO powder with Cu. Consequently, with a weight ratio of 1:1, the intentionally Cu-doped ZnO powder and the graphite power (99.99%, Aldrich) were mixed together and ground for 0.5 h. This batch samples were named S-1.

For the 2nd synthesis scheme, the source is the mixed powders of undoped ZnO with graphite. Si and a-plane Al₂O₃ substrates were utilized for the 1st and 2nd schemes, respectively. As NWs growth catalyst, a thin (1-2 nm) layer of Au was coated on substrates, then the substrates were placed at the particular position into quartz tube for growth. The growth temperature was kept at ~960 °C. The mixed gas of Ar and O₂ with the flow rate of 47.5 sccm and 2.5 sccm was used as a carrier gas. After undoped ZnO NWs growth, a 2 nm layer of Cu was sputtered onto the surface of the vertically aligned NWs,

followed by a thermal treatment in air for 8 hours at temperatures between 600 and 800 °C. This batch of samples was named S-2.

In terms of samples crystal, chemical and magnetic properties investigation, the experimental setup and characterization details were described in earlier **Chapter 2**. Only plastic tweezers were employed to avoid any unintentional contamination with magnetic metals, throughout all the experimental steps conducted during growth and measurements.

§4.1.3 Morphology, microcosmic structure and composition results²¹

SEM, XRD, Raman, TEM, EDS, XPS and SIMS results

The critical experimental conditions and results of the 2 synthesis schemes are listed in **Table 4-1**. Such 2 different synthesis approaches were designed aiming to yield dissimilar amounts of structure inhomogeneity. For the 1st scheme, Cu-doped ZnO powder was synthesized first by a conventional solid state reaction method to achieve a homogeneous dopant distribution. Then the doped NWs (S-1) were fabricated by a chemical vapor transport approach.^{88, 89}

Table 4-1. Experimental conditions and outcomes of the 2 growth approaches.

Sample Type	Source Powders for NW growth	Doping route	Cu doping concentration	Cu distribution	Magnetization
S-1	Zn _{1-x} Cu _x O/C	Solid state reaction	~4.9%	Homogeneous	Weaker
S-2	ZnO/C	Coating Cu layer and followed by annealing treatment	~2.2%	Inhomogeneous	Stronger

Figure 4-1 (a) shows the SEM image morphology results of the as-fabricated NWs (S-1), the diameter of NWs is ranging from ~40 nm to ~90 nm and the length is a few μm . As can be seen from **Figure 4-1** (b), the SAED pattern result indicates that the sample S-1 can be indexed as the wurtzite hexagonal ZnO structure that is free of secondary phase, suggesting that there is no Cu related compound phases. The HRTEM image [**Figure 4-1** (c)] indicates that the NWs growth is along the [001] direction, in a good agreement with the previously reported results from undoped ZnO nanowires.^{88, 89} We carried out extensive HRTEM experiments and all obtained results suggest that a uniform Cu dopants distribution was achieved without metal clustering or precipitates formation.

Figure 4-1. (a) SEM image of Cu-doped ZnO NWs (S-1) synthesized by evaporating and transporting vapors from $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ powder. (b) SAED pattern, and (c) HRTEM image of an individual NW.

Figure 4-2. (a) XRD patterns of sample S-1. (b) XPS detailed scan of Cu 2p_{3/2} and 2p_{1/2} core-level peaks obtained on sample S-1.

The x-ray diffraction patterns obtained from sample S-1 [Figure 4-2 (a)] can be identified as the hexagonal wurtzite ZnO structure. There is no impurity peak observed, consistent with the SAED and the HRTEM results. Inset, the (002) peak shifts toward the higher diffraction angle due to the smaller ion radius of Cu²⁺ (0.057 nm) than that of Zn²⁺ (0.060 nm).

Figure 4-3. XPS survey scan spectrum taken on S-1.

XPS was employed to verify the Cu doping concentration and the chemical valence states of Cu. The survey scan (**Figure 4-3**) indicates that no magnetic impurity was observed, and after calculation, the atomic composition percentages on sample surface are determined to be 51, 44.1 and 4.9, for Zn, O, and Cu, respectively. As shown in **Figure 4-2 (b)**, the Cu $2p_{3/2}$ and $2p_{1/2}$ peaks are placed at 933.38 eV and 953.17 eV, respectively, analogous to the reported results from ZnO nanocrystals doped with Cu.^{90,91} A Gaussian fitting method helps to determine the ratio of $\text{Cu}^{1+}/\text{Cu}^{2+}$ to be 19.6:80.4, similar to the previously reported results.^{90,91} Different from Cu^{2+} ions, Cu^{1+} 3d orbitals are fully filled and hence don't contribute to FM.

Figure 4-4. (a) SEM image of vertically aligned Cu-ZnO NWs (S-2). (b) HRTEM image of an individual as-fabricated NW after coating a Cu layer via sputtering. (c) HRTEM image of a 600 °C annealed NW sample (S-2). (d) HRTEM image of an 800 °C annealed NW, indicating a deformed domain enclosed by 2 dashed lines.

Compared with the 1st synthesis scheme, the 2nd one featured samples with a stronger structure inhomogeneity. Vertically-aligned ZnO NWs were first grown on a-plane Al₂O₃ substrate and then a ~2 nm Cu was sputtered onto the NWs. Such method was aroused by Chai *et al.*⁹² **Figure 4-4** (a) shows a SEM image of S-2 NWs with the diameter around 120-400 nm and the length of ~4 μ m in dimension. Cu doping was realized by annealing ZnO/Cu NWs with a core/shell structure in the temperature of 600 ~ 800 °C. The vertical alignment of ZnO NWs on the Al₂O₃ substrates renders a homogeneous Cu coating onto the sidewalls of NWs. The shell structure of Cu layer has a thickness of ~2 nm [**Figure 4-4** (b)]. After annealing at both temperature points of ~600 and ~800 °C, the HRTEM results as shown in **Figures 4-4** (c) and (d) indicate that the extinguishment of the Cu shell was accompanied by the production of a large amount of defects and distorted domain structures. As to the sample annealed at 600 °C (S-2), such defect-forming tendency is dramatically enhanced especially in the surface region of NW by the Cu diffusion process. As shown in **Figure 4-4** (c), a line up multiple stacking faults formation with dim contrast. Similar results were obtained for the samples annealed at 800 °C [**Figure 4-4** (d)] and also show a distorted domain structure in nanoscale.

The XRD data of S-2 [**Figure 4-5**] show a dominant ZnO (002) peak. And a very weak Cu (111) peak appeared after Cu layer coating action. Apparently the extinguishment of this Cu (111) peak through the annealing treatment suggests that Cu atoms occupied the Zn lattice sites in the ZnO matrix. Furthermore, the EDS spectroscopy results [**Figure 4-6**] obtained before and after the thermal annealing are coherent with the XRD data. The calculated chemical composition percentage based on the obtained XPS

data [Figure 4-5 (b) and inset] are 62.4, 35.4, and 2.2, for Zn, O, and Cu, respectively.

Thus, the Cu content in sample S-2 is less than that in sample S-1.

Figure 4-5. (a) X-ray diffraction patterns of S-2. (b) XPS survey scan and detailed scan (inset) of Cu 2p_{3/2} and 2p_{1/2} core-level peaks taken on S-2.

Figure 4-6. EDS spectrum taken on S-2. The inset depicts the Cu peak disappeared after annealing treatment.

Figure 4-7. SIMS spectra data taken on S-1 and S-2. With a complex configuration of NWs, the “depth” might not represent the actual thickness of the samples.

Figure 4-8. (a) XRD patterns taken on S-1, S-2 and CuO film with a 2 nm thickness. (b) Raman spectra measured on samples S-1, S-2, pure ZnO NWs, and a 2 nm thick film.

The SIMS study also verified the lower doping concentration and the inhomogeneous distribution of Cu in S-2 [Figure 4-7]. Only elements of Zn, O, and Cu were detected. Due to the element dependent ion-sputtering yields, the composition of samples cannot be determined quantitatively by the measured intensities; apparently, for both samples, the intensities of oxygen are higher than those of Zn although the samples are oxygen deficient. The Cu concentration in S-1 tends to be higher than that in S-2,

consistent with the XPS results. The observation of more inhomogeneous distribution and a lower concentration of Cu in S-2 are in a good agreement of the above discussion.

Moreover, extensive XRD and Raman measurements were carried out on samples S1 and S-2 and there was no Cu-related secondary phase observed within the detection limits [Figure 4-8].

§4.1.4 Comparative magnetic properties characterization²¹

SQUID results

Figure 4-9. *M-H* raw data without any subtraction of the substrate signals taken on sample S-1 (a) and sample S-2 (b). (c) and (d) show the diamagnetic signals of Si and Al_2O_3 substrates, respectively.

The different structural characteristics and Cu concentrations in S-1 and S-2 motivated us to investigate their magnetic properties via a comparative study. After

consideration on the previous reports of weak FM in Si and Al_2O_3 substrates,⁹³ firstly, we measured the magnetic characteristics of the Si and the Al_2O_3 substrates. Both of them showed only diamagnetic signals as shown in **Figure 4-9**.

Figure 4-10. (a) M - H data measured at 5 K and 300 K. (b) M - T curves of the samples under a magnetic field of ~ 500 Oe.

The backgrounds of the Si and Al_2O_3 substrates were subtracted from the raw data.

Figure 4-10 (a) shows M - H data obtained on samples S-1 and S-2 at 5 and 300 K, both samples exhibit clear hysteresis loops which suggest RTFM. The saturation magnetization is about 3 kOe, which is slightly higher than that of reported results from thin films.^{94, 95} A noticeable characteristic in our results is that the magnetization of S-2 is about 10 times stronger than that of sample S-1. Aiming to eliminate the potential effect from unintentional contaminants, as shown in **Figure 4-11** (a), we measured a sample coated with Cu but without annealing treatment and found that there is no FM. Thus we can come to a conclusion; the enhanced FM in S-2 cannot be ascribed to magnetic impurities that might be introduced during the coating processes. The boosted RTFM is fairly robust

and confirmed also in the annealed sample at 800 °C [Figure 4-11 (b)]. Therefore, after Cu coating and accompanied annealing treatment, sample S-2 exhibited a much stronger FM than S1 although it possesses less Cu content.

Figure 4-11. (a) Diamagnetic M - H data measured on a sample coated with Cu without annealing. (b) M - H data taken on the 800 °C annealed sample at 5 and 300 K.

M - T data were measured under a 500 Oe B field with both zero field cooled and field cooled modes. Consistent with the M - H results, the temperature dependent magnetization of sample S-2 is much higher than that of sample S-1. The magnetization of S-2 increases continuously as the temperature decreases, consistent with the previously reported results in DMS thin film samples.^{90, 96} At lower temperatures, both S-1 and S-2 show the Curie-Weiss type behaviors, indicating the existence of a paramagnetic phase. Such component with paramagnetic behaviors is likely due to the Cu 3d electrons

localization and the dynamic Jahn-Teller effect.^[9] With a trigonal crystal field, the dominant Cu^{2+} ions observed in our XPS study, support the Jahn-Teller distortion.⁹⁷ We found that the absence of blocking behavior in the ZFC curves excludes the existence of magnetic nanoclusters,⁹⁸ in accordance with the theoretical calculation.⁹⁹ Finally, the M - T feature at around 50 K might originate from the magnetic transition behavior of oxygen contaminants.¹⁰⁰

Magnetic Force Microscopy (MFM) results

Figure 4-12. (a) Topography morphology and (b) MFM images of an individual S-1 NW. (c) Topography morphology and (d) MFM images of an individual S-2NW. All the scanning areas are $5\ \mu\text{m} \times 5\ \mu\text{m}$.

The enhanced RTFM was further verified by the RT MFM measurements. As to both S-1 and S-2, the topographical morphology and the associated MFM images were obtained with scanning area of $5\ \mu\text{m} \times 5\ \mu\text{m}$. In **Figure 4-12** (b), there is no clear phase contrast was observed in S-1, suggesting a weak magnetism beyond the detection capability of setup. However, with the same scanning environment and conditions, sample S-2 exhibits a clear magnetic response as shown in **Figure 4-12** (d). Such contrastive results are good in agreement with the SQUID results and exclude the perturbation from the MFM probe. In **Figure 4-12** (c), after drop casting there are many residual particles with comparable heights to the NW. But, these contaminants show no magnetic contrast as indicated in **Figure 4-12** (d), which further sustains the intrinsic nature of the enhanced RTFM in S-2.

§4.1.5 Discussions on RTFM mechanisms

The observed enhanced RTFM in S-2 is highly correlated with the structural inhomogeneity. Such correlation favors the bound magnetic polarons (BMP) formation as the origin of observed RTFM. The enhanced RTFM by structure defects has been previously reported in Cr- and Cu-doped ZnO thin films and Ni-doped ZnO nanocrystals.¹⁰¹⁻¹⁰³ Durst *et al.* claimed that defects tend to increase BMPs formation that couple with $3d$ orbitals moments.¹⁰⁴ The magnetic polarons overlapping causes spin-spin interactions between magnetic ions and eventually stabilize the ferromagnetic ordering. Different from the carrier-mediated mechanism, BMP can induce RTFM even in the insulating DMS samples with low carrier concentrations. For S-2, the structure defects as

a result of Cu diffusion generate a larger overall volume occupied by BMPs, hence fostering the creation and percolation of ferromagnetic domains.¹⁰⁵ The localization of defects from TEM data, suggest that RTFM is a surface effect by nature, but not a homogeneous bulk behavior. Unlike the conventional double exchange or superexchange interaction, the electronic structure alteration induced by defects and impurities plays a paramount important role in the onset of the observed FM.⁶⁷

§4.1.6 Summary

In summary, we performed a comparative study on Cu-doped ZnO NWs fabricated by two distinct strategies and demonstrated clearly an enhanced RTFM by structural inhomogeneity. In addition to the dopant concentration, modulating the structural and the electronic properties should be an alternative route to manipulate the ferromagnetic properties of NWs. Such strategy may eventually promote the use of DMS NWs as building blocks in spintronic devices.

§4.2 Carriers and Exciton Spin Dynamics in Cu-ZnO Nanowires

§4.2.1 Introduction

To avoid the issues of secondary magnetic phases or metal precipitates giving rise to extrinsic FM in DMS, doping of non-magnetic metallic elements such as Cu were attempted. Cu atoms do not have clustering inclinations and the Cu-based compounds are

non-ferromagnetic.⁸³ ZnO doped with Cu material system has great potential for further development in semiconductor spin-based applications.^{64, 86}

Highly spin-polarized carriers with long spin decay lifetimes are necessary criteria for the transfer and manipulation of spin information in practical spintronic devices. Ghosh *et al.*¹⁰⁶ investigated the electron spin properties in n-type ZnO bulk and epilayer samples and reported that the electron spin coherence time T_2^* varies from 20 ns to 190 ps (from 10 to 280 K). Room-temperature electron spin relaxation of 25 ns, measured by electron paramagnetic resonance in ZnO quantum dots has also been reported.⁸⁶ Recently, Largade *et al.* reported on the exciton and hole spin dynamics in bulk and epilayer ZnO¹⁰⁷ and the hole spin quantum beats in bulk ZnO.¹⁰⁸ However, to the best of our knowledge, there have been no reports on the carrier spin dynamics in ZnCuO. It is therefore of our interest to investigate the transient spin behavior of these carriers using optical orientation studies.

Despite its promising properties, there are several issues¹⁰⁹ pertaining to both spin injection and spin detection in ZnO-based materials. Spin injection from an adjacent magnetic layer has been unsuccessful.^{109, 110} Optical techniques require near-UV resonant optical excitation of the excitons due to the weak spin-orbit coupling energy (9–16 meV) in ZnO.¹¹¹ The efficiency of optical spin detection in ZnO is affected by issues of weak spin-orbit coupling and efficient carrier/exciton spin relaxation in this system.¹⁰⁹ In this section, we report on the observations of long-lived ($\tau_e^s > 1.5$ ns at temperature $T = 5$ K), highly spin-polarized acceptor bound exciton emissions ($P_{ini} \sim 65\%$) from ZnCuO NWs, following optical spin injection under zero external B-field. This work demonstrates that highly spin-polarized emissions in ZnO-based materials can be achieved through doping

and band structure modulation.

§4.2.2 Experimental details

NWs Fabrication and Characterization:

As-fabricated NWs show the dimension with a diameter of 40–90 nm and a length of a few micrometers. The FFT pattern indicates that the Cu-doped ZnO NWs can be indexed as the wurtzite hexagonal structure with no detectable secondary phase, which is consistent with the XRD results. The HRTEM images show that the NWs grow along the [0001] direction. Extensive HRTEM observations were taken on several samples. The chemical bonding states and the compositions of the products were determined by XPS. The Cu doping concentration was determined to be around 2 at.% accompanied with substantial oxygen deficiency.

Optical Measurements:

Low temperature time-integrated photoluminescence (TIPL) measurements were performed using a cw He-Cd laser operating at 325 nm. The steady-state luminescence from the sample was dispersed by a 750 mm monochromator, and detected by a photomultiplier using the standard lock-in amplifier technique. For the transient spin-polarized optical orientation experiments, the excitation laser pulses were generated from an optical parametric amplifier (OPA) that is pumped by a 1kHz, 800 nm, 100 fs pulses from a Coherent LegendTM regenerative amplifier (that was seeded by a Coherent VitesseTM Ti-sapphire oscillator). The UV pulses from the OPA were dispersed using a prism and spectrally collimated using a pair of slits to a bandwidth of 1.2 nm (FWHM). Thus, quasi-resonant excitation of the acceptor bound excitonic level using narrow

bandwidth circularly polarized laser pulses could be realized. Circularly polarized (σ^+ or σ^-) pulses were generated using a Soleil-Babinet compensator (SBC). The co-polarized I^+ and counter-polarized I^- (with respect to the polarization of the σ^+ excitation source) PL emission was collected in a conventional backscattering geometry and was spectrally dispersed by a DK240 1/4 m monochromator with 150 g/mm grating. The signal was temporally resolved by the Optronis OptoscopeTM streak camera system. A fast triggered sweep unit (Optronis FTSU1-ST) with an ultimate temporal resolution of 10 ps was used for the data collection. The streak camera and the laser source were electrically synchronized. The streak camera images were recorded using a 12-bit cooled CCD readout unit (Optronis SCRUI-SE) and the data was averaged over 500 accumulated images. The PL decays were extracted at the acceptor bound exciton (A^0X) peak. Extreme care was taken to correct for the polarization dependence of the gratings in the spectrograph. The PL polarization degree is defined in percentage as $P_c = 100(I^+ - I^-)/(I^+ + I^-)$. Excitation fluence was kept to $\sim 80 \pm 10$ nJ/cm² per pulse to avoid any multiphoton effects and damage to the NW samples.

Samples of undoped ZnO and ZnCuO well aligned NWs were synthesized using a chemical vapor transport method²¹ on a Sapphire substrates. Homogenous Cu-doping was achieved and the doping concentration was determined to be ~ 2 at.% by x-ray photoelectron spectroscopy. These ZnCuO NW samples exhibit room-temperature FM.²¹ Cu-doping modulates the band structure of ZnO. First principle calculations of the electronic structure of Cu-doping in ZnO showed that the Cu 3d bands are strongly hybridized with the O 2p levels and the Zn 3d levels are located in the region of ~ 5 eV below the Fermi level.^{112, 113} From band structure calculations, Lambrecht *et al.* showed

that both the crystal field and spin orbit splittings have a strong dependence on the position of the d bands (e.g. for Zn 3d bands at 5.5 eV, $E_{AB} \sim 25$ meV and $E_{BC} \sim 60$ meV).¹¹⁴

Figure 4-13. (a) XRD pattern of ZnCuO NWs sample, the inset shows a shift of the (002) peak compared with the pure ZnO sample. Representative (b) low and (c) high resolution TEM images of an individual NW. Inset shows the corresponding fast Fourier transformation (FFT) pattern.

§4.2.3 Steady state and dynamic optical properties study

Thus, quasi-resonant excitation of the acceptor bound excitonic level could be realized. The co-polarized I^+ and counter-polarized I^- emissions (with respect to the polarization of the σ^+ excitation source) were collected in a conventional backscattering geometry and dispersed by a spectrometer. The transient luminescence was detected by a

S-25 photocathode streak camera with a temporal resolution of 10 ps. The PL decays were extracted at the acceptor bound exciton (A^0X) peak. The PL polarization degree is defined in percentage as $P_e = 100(I^+ - I^-) / (I^+ + I^-)$.

Figure 4-14. Schematics of the conduction band (CB) and valence band (VB) states in wurtzite ZnO with (a) a normal and (b) an inverted valence band. Spectrally collimated right circularly-polarized (σ^+) laser pulses were used to resonantly excite the $\Gamma_{9/7}^v \leftrightarrow \Gamma_7^c$ transition. Herein, the spin up electrons in Normal VB and spin down electrons in the inverted VB are taken as examples.

Figure 4-14 shows a schematic of the conduction band (CB) and the top of the valence band (VB) of ZnO comprising of the A, B and C states for both the normal and inverted A-B structure whose exact nature is still unresolved.^{111, 115} The $\Gamma_{9/7}^v \leftrightarrow \Gamma_7^c$ transition was quasi-resonantly excited using spectrally collimated right circularly-polarized (σ^+) laser pulses.

Figure 4-15 (a) shows the temperature-dependent emission spectra of ZnCuO NW samples from TIPL measurements. The spectra exhibit several emission peaks identified to be originating from the free excitons (FX), acceptor bound excitons (A^0X) and their corresponding replicas.^{3, 8} As temperature increases, the intensity of the A^0X emission (at 3.353 eV) decreases and the peak position redshifts. The decrease in PL intensity is due to the dissociation of A^0X into the neutral acceptor (A^0) and FX. **Figure 4-15** (b) shows the Arrhenius plot of the A^0X integrated intensity as a function of $1000/T$. The solid line is the least square fit of the data with the equation: $I(T) = I_0 / (1 + A e^{(-E_b / k_B T)})$, where the activation energy, E_b is ~ 21.8 meV. From Haynes's rule,¹¹⁶ this value corresponds well to the 10% of the energy level of the (Cu^+ , hole) in ZnO. The A^0X emission is most likely to originate from the bound exciton complex formed at the (Cu^+ , hole) acceptor level located near the top of the VB of ZnO.^{8, 117} Different from Cu^{2+} ions, Cu^{1+} 3d orbitals ($3d^{10}4s^0$) are fully filled and hence do not contribute to FM. No net spin polarization can be detected when linearly polarized excitation pulses (with $B = 0$ T and $T = 5$ K) are used instead, which rules out the possibility of spin alignment.

Figure 4-15. (a) Temperature-dependent PL spectra of ZnCuO NWs under 325 nm light excitation. (b) The Arrhenius plot of the integrated PL intensity of the A^0X emission as a function of $1000/T$.

Figure 4-16. Temporal evolution of the circular luminescence I^+ and I^- components following σ^+ excitation on ZnCuO NWs sample. Luminescence from the A^0X state originates from a hole singlet and an electron: $|h\downarrow, h\uparrow, e^-\downarrow\rangle$. Inset shows the schematic of the spin states for the A^0X , $\downarrow, \uparrow$: electron spin, $\downarrow, \uparrow$: hole spin.

The PL circular polarization dynamics was monitored at the A^0X peak (3.353 eV) upon right circularly-polarized σ^+ excitation of the ZnCuO NWs sample at 5 K (**Figure 4-16**). The excitation energy was tuned to 14 meV above the A^0X emission peak and below the FX energy level. The luminescence from the A^0X state arises from a hole singlet and an electron: $|h\downarrow, h\uparrow, e^-\downarrow\rangle$ as shown in the inset of **Figure 4-16**. Hence, the measured PL circular polarization monitors the degree of the electron spin polarization.⁶⁴

The initial polarization $P_{ini} \sim 65\%$ was measured at 200 ps after the laser excitation

to minimize the effects of backscattered laser light from the NWs sample. It is surprising that despite the high defect densities in ZnCuO NWs, this high degree of spin polarization was found to persist longer than 1.5 ns. To the best of our knowledge, this measured value of ~65% spin polarized emission from a ZnO-based material (following optical spin injection at $B = 0$ T) is the highest reported to date. As a check on self-consistency, optical orientation experiments using the same setup were also performed on the undoped ZnO NWs, monitoring the donor bond exciton emissions. The measured values of hole spin relaxation time, $\tau_h^s \sim 315$ ps and $P_{ini} \sim 18\%$ at 16 K are consistent with those reported by Lagarde *et al.*¹⁶ for ZnO epilayers (**Figure 4-17**).

Optical orientation experiments using the same setup were also performed on undoped ZnO NWs. In this case, the spin dynamics of the donor bound excitons D_1^0X were monitored. The excitation energy was tuned to be 12 meV above the D_1^0X emission peak at 3.357 eV. Representative data of the PL circular polarization dynamics are shown in **Figure 4-17**. These values are consistent with those reported by Lagarde *et al.*¹⁰⁷ for ZnO thin films.

Figure 4-17. (a) Temperature dependent PL spectra of undoped ZnO NWs under 325 nm

light excitation. (b) Temporal evolution of the circular luminescence I^+ and I^- components following σ^+ excitation of the undoped ZnO NWs sample. (c) Excitation energy dependence of the D_1^0X excitons initial circular polarization P_{ini} as a function of the energy difference ΔE at 16 K for the undoped ZnO NWs.

Figure 4-18. (a) Excitation energy dependence of the initial circular polarization P_{ini} of the A^0X exciton as a function of the energy difference ΔE at $T = 16$ K. (b) Temporal evolution of the circular polarization at different temperatures. Straight lines are the linear fits with a mono-exponential function.

Figure 4-18 (a) shows a plot of the spectral dependence of the A^0X circular polarization P_{ini} against the energy difference $\Delta E = E_{exc} - E_{det}$, where E_{exc} is the excitation energy and E_{det} is the detection energy. The time dependent circular polarization dynamics measured at different temperatures are plotted in **Figure 4-18** (b). The PL

circular polarization dynamics at higher temperatures (i.e. $T > 25$ K) were fitted using a mono exponential decay and the temperature dependence of the electron spin relaxation time τ_e^s is plotted in **Figure 4-18** (a). As the temperature increases, the bound acceptor excitons could gain sufficient energy to dissociate into the neutral acceptor and FX. The FX loses its spin orientation, and upon trapping at the acceptor sites, the initial spin orientation of the electron and hole (of the exciton) would be lost,¹³ resulting in the fast decrease of the polarization decay time. Further investigations are ongoing to investigate the spin dephasing time in these ZnCuO NWs.

§4.2.4 Summary

In conclusion, Cu-doped ZnO NWs investigated using transient spin-polarized optical orientation measurements were found to exhibit long-lived ($\tau_e^s > 1.5$ ns) highly spin-polarized excitonic emissions ($P_{ini} \sim 65\%$) following optical orientation under zero external B-field. These emissions originate from the acceptor-bound excitons (A^0X) – likely from the (Cu^+, h) state. This work is a proof of concept that highly spin-polarized emissions in ZnO-based materials can be achieved through doping and band structure modulation. Such 1D nanostructures which exhibit long-lived and highly spin polarized emissions characteristics may find potential applications as spin-polarized LED and lasers devices.^{3,8} For example, as a *p*-type conductive semiconductor with high spin-polarized carriers, Cu-doped ZnO NWs layer is highly potential for constructing magneto-optical spin-polarized homo-*pn*-junction. Briefly, the spin polarized electrons or holes from *n*-type and *p*-type doped magnetic ZnO are injected into intrinsic ZnO region and

recombine with the unpolarized hole or electrons from the p - or n -ZnO layer, consequently the resulting recombination light can be significantly enhanced due to initially spin polarized carriers. Hence, the oriented spins are converted into photons of light. It is desirable to use undoped ZnO as a recombination region layer to overcome the limit of injection efficiency due to the inelastic conduction. Such an all ZnO thin films based homo- pn -junction will be very unique and fairly feasible.

Chapter 5 Strong Correlation between Oxygen Deficiency and Ferromagnetism in Diverse $\text{In}_2\text{O}_{3-\delta}$ Nanostructures Doped with Chromium

§5.1 Introduction to In_2O_3 based DMS systems

As a popular transparent oxide semiconductor, In_2O_3 (IO) has a body-centered cubic structure and a direct wide band gap of ~ 3.75 eV. Moreover, nowadays, IO-based DMS has gained numerous attention and RTFM was previously reported in IO compound doped with V, Fe, Mn, Ni and Cr.¹¹⁸⁻¹²² Among these elements, Cr dopant is especially intriguing and has attracted a lot of interests.¹²³⁻¹²⁷ Cr-doped IO (Cr:IO) thin films with the T_c of 850 K was reported in 2006.¹²³ Cr element is antiferromagnetic and it would not induce any extrinsic FM even if the Cr clustering formation happens. Moreover, Cr^{3+} ions present high-spin configuration $3d^3$, which might be helpful to create large magnetic moments in the host. Most previous studies of doped IO focus on bulks or thin films; only few works have been reported so far on 1D IO-based DMS materials.

In present Chapter, I performed a systematic study on the magnetic properties of diverse Cr:IO nanostructures prepared by vapor transport growth. By optimizing the growth conditions, I synthesized IO and Cr doped counterpart nanostructures with diverse morphologies including nanotowers (NTs), nanowires (NWs), and octahedrons, RTFM was observed in the as-grown samples with sufficient oxygen deficiency regardless of the morphology structures, and the FM was dramatically deteriorated upon annealing

treatment in atmosphere, which indicates that there is a strong correlation between the oxygen deficiency and the FM. The origin of the observed FM was proposed to involve the defect assisted BMPs creation and the doping induced alteration of the electronic band structure for host.²³

§5.2 Experimental details

Three categories of Cr:IO nanostructures, i.e., NTs, NWs and octahedrons were prepared by chemical vapor transport method. The detailed experimental setup was described in **Chapter 2**. Used as the source for the growth of Cr:IO NTs and NWs, In_2O_3 (Sigma Aldrich, 99.999%), C (Sigma Aldrich, 99.99%) and CrCl_2 (Sigma Aldrich, 99.99%) powders with a weight ratio of 5:4:0.6 and 0.1 g in total weight were mixed and ground for 20 min. 0.5% O_2 mixed with Ar was used as the carrier gas and the flow rate was kept at ~80 sccm. The growth pressure is maintained at ~100 torr. The growth temperature was increased to 980 and 800 °C, which led to the production of NTs and NWs, respectively. As to Cr:IO octahedrons synthesis, a mixture of In (Sigma Aldrich, 99.999%) and CrCl_2 powders was used as the source and the growth temperature was ~980 °C. As to the undoped IO samples synthesis, all the experimental conditions are identical except that CrCl_2 was not used in the source. Total growth time was around 1 hour, and then the furnace was cooled down naturally to RT.

The characterization details were described in earlier **Chapter 2**. For XPS measurements, the chemical compositions were determined by fitting to the integrated intensities of the core level peaks and using the calibrated atomic sensitivity factors ($\text{In}3d5$: 6; $\text{Cr}2p$: 2.3; $\text{O}1s$: 0.66). Magnetization measurements were carried out by

employing a SQUID setup.

§5.3 Physical properties of Cr:IO nanostructures²³

Table 5-1. Chemical compositions and morphologies of the Cr:IO and IO nanostructures with and without annealing treatments.

Sample	Morphology	Composition	Annealed
CIO-T1	NTs	$(\text{In}_{0.97}\text{Cr}_{0.03})_2\text{O}_{2.57}$	No
CIO-T2	NTs	$(\text{In}_{0.97}\text{Cr}_{0.03})_2\text{O}_{2.88}$	Yes
IO-T1	NTs	$\text{In}_2\text{O}_{2.57}$	No
CIO-W1	NWs	$(\text{In}_{0.97}\text{Cr}_{0.03})_2\text{O}_{2.28}$	No
CIO-W2	NWs	$(\text{In}_{0.97}\text{Cr}_{0.03})_2\text{O}_{2.55}$	Yes
IO-W1	NWs	$\text{In}_2\text{O}_{2.29}$	No
CIO-O1	Octahedrons	$(\text{In}_{0.97}\text{Cr}_{0.03})_2\text{O}_{2.40}$	No
CIO-O2	Octahedrons	$(\text{In}_{0.97}\text{Cr}_{0.03})_2\text{O}_{2.80}$	Yes
IO-O1	Octahedrons	$\text{In}_2\text{O}_{2.42}$	No

In this Chapter I will concentrate on the experimental results obtained from NTs because that the experiment procedures and physical characterizations are similar to all samples. The oxygen content in the NTs was adjusted by annealing the as-grown samples at 600 °C in air for 1 hour. As itemized in **Table 5-1**, the as-grown and the post annealed Cr:IO NT samples were named as CIO-T1 and CIO-T2, respectively.

As can be seen in **Figure 5-1** (a), the tower-like nanostructures were synthesized on the Si substrates and the observed four-fold symmetry is in good agreement of the IO bixbyite structure. Compared with the undoped IO samples, Cr doping doesn't change the product morphology. It is well-known that the growth rate perpendicular to different

planes is proportional to their surface energies. The catalyst droplet continually dissolved and adsorbed the vapor phase reagent species, initiating the growth of nanoplate first, and then the periodical 1-D and continuous 0-D growth finally resulted in the formation of NT structures.

Figure 5-1. Low (a) and high (b) magnification SEM images of Cr:IO NTs. HRTEM images obtained at the tip (c) and the side (d) of an individual NT and associated SAED patterns (e).

HRTEM technique was employed to investigate the structural characteristics of the Cr:IO NT samples in detail. As shown in **Figure 5-1** (c), the smooth top surface likely suggests the Au migration behavior during the VLS growth process.^{128, 129} Apparently, the NTs grow along the [100] direction, in accordance with the previous reports on undoped

IO NTs.¹³⁰ The side surfaces reconstruct into $(\bar{1}1\bar{1})$ and $(11\bar{1})$ facets [Figure 5-1 (d)] as a result of the slower growth rate along $\langle 111 \rangle$ than that of those along $\langle 100 \rangle$ and $\langle 110 \rangle$ directions. As can be seen in Figure 5-1 (e), the SAED pattern taken along the $[0\bar{1}\bar{1}]$ zone axis suggests a cubic structure without secondary phase.

Figure 5-2. (a) XRD patterns of the as-grown Cr:IO NTs CIO-T1. Inset depicts the (222) peaks of CIO-T1, CIO-T2 and the undoped (IO-T1) samples. (b) XPS survey spectra

taken on the samples CIO-T1 and CIO-T2. Insets are the high resolution scans of Cr $2p_{3/2}$ and $2p_{1/2}$ peaks. Wherein, the solid lines and circles indicate the data taken before and after the sputtering, respectively. (c) Raman spectra taken on the CIO-T1 and CIO-T2. Solid circles represent the IO phase [dash line] and solid squares correspond to the Si substrates.

In **Figure 5-2** (a), the XRD pattern of CIO-T1 indicates the cubic bixbyite structure without any impurity phase, which is in accordance with TEM data. The (222) peak of CIO-T1 shows a shift of 0.06° towards a larger angle compared with the undoped IO NTs (IO-T1), which ascribes to a shrinkage of lattice constant after doping of the smaller Cr^{3+} ions ($0.76 \text{ \AA}$) compare with the In^{3+} ($0.94 \text{ \AA}$),¹³¹ which suggests that Cr ions occupied the In ions lattice sites in IO matrix. There is no introduction of any new phase in CIO-T2 even upon annealing treatment. The (222) peak in CIO-T2 is slightly narrower than that of CIO-T1, which suggests an improved crystal structure after annealing treatment.

XPS measurements were carried out on the NT samples to investigate the compositions and the chemical valence states. Firstly, the Ar ion sputter cleaning treatment was performed to eliminate any potential surface contamination. As shown in **Figure 5-2** (b), the survey scans of CIO-T1 and CIO-T2 show no magnetic impurity above the detection limit. $\text{Cr}2p_{3/2}$ peaks located at 577.50 and 577.20 eV were observed for CIO-T1 and CIO-T2, respectively. The peak positions are different from Cr^{2+} (576.0 eV), Cr^{4+} (576.30 eV), Cr metal (574.0 eV) and Cr^{6+} ions (579.0 eV), but match Cr^{3+} ions (577.20 eV).¹³² The eventual nonstoichiometric formula for CIO-T1, and CIO-T2 were determined to be $(\text{In}_{0.97}\text{Cr}_{0.03})_2\text{O}_{2.57}$ and $(\text{In}_{0.97}\text{Cr}_{0.03})_2\text{O}_{2.88}$, respectively. We noted that the

doping route consistently led to a ~3 at. % Cr content.¹²³ It is notable that substantial oxygen vacancy defects exist in Cr:IONT samples. Air annealing significantly decreases the oxygen deficiency to 4% and increases the oxygen content by ~12% in CIO-T2.

The extrinsic sources like secondary phases or ferromagnetic clusters may cause RTFM. Raman spectroscopy studies [Figure 5-2 (c)] were performed and no Cr-related secondary phase was observed in CIO-T1 and CIO-T2, within the detection limit. The characteristic Raman modes located at 308.0, 368.0, 498.50 and 628.50 cm^{-1} ; all the detected modes match well with the frequencies as previously reported in cubic In_2O_3 .¹³³

Figure 5-3. PL spectra of CIO-T1 and CIO-T2 obtained at RT.

The oxygen deficiency defects strongly affect the optical properties in IO-based samples. As can be seen from Figure 5-3, CIO-T1 and CIO-T2 show broad orange-red emission band peaked at around 640 nm, which was ascribed to oxygen vacancies.¹³⁴ Previous theoretical computations suggested that the considerable oxygen deficiency in IO should be recognized as oxygen vacancies but not cation interstitials.¹³⁵ In contrast

with CIO-T2, the stronger visible emission in as-grown CIO-T1 suggests its substantial oxygen deficiencies, which verifies the XPS data. The appearance of 2 peaks at 413 and 444 nm in CIO-T2 might be associated with the near band edge emission,¹³⁶ indicates an improved crystal structure and fewer defects in CIO-T2, in good agreement with the XRD data.

Figure 5-4. (a) $M-H$ raw data without the deduction of the substrate signal measured on as-grown Cr:IO NT sample CIO-T1. (b) $M-H$ data taken on a Si substrate showing the diamagnetic behaviors. (c) $M-H$ data of the as-grown CIO-T1 and the annealed sample CIO-T2 taken at 5 and 300 K. (d) ZFC and FC $M-T$ curves of the as-grown CIO-T1 and the annealed CIO-T2 samples.

The magnetic measurements were conducted by using a SQUID magnetometer.

Without subtracting the substrate contribution, M - H raw data were measured at 5 and 300 K for CIO-T1 and CIO-T2 [Figure 5-4 (a)]; indicating that a ferromagnetic component exist in M - H loops. Aiming to exclude any potential contamination effect of the substrates, as shown in Figure 5-4 (b), the blank substrate were measured and shows only diamagnetic behaviors.

After diamagnetic backgrounds deduction of the Si substrates according to the sample weights, Figure 5-4 (c) shows the M - H curves measured at 5 and 300 K for CIO-T1 and CIO-T2. Both samples show clear M - H hysteresis loops, demonstrating RTFM. As to the as-grown CIO-T1, the coercivity and the saturation magnetization at 300 K are ~ 59 Oe and $\sim 0.81 \mu_B/\text{Cr}$, consistent with the previously reported results taken on Cr:IO thin films with oxygen-deficiency.¹⁸ Under 500 Oe field, the zero field cooled and the field cooled measurements were carried out [Figure 5-4 (d)]. We essentially found that the magnetic properties are highly associated with the oxygen concentration: the room temperature saturation magnetization of CIO-T1 is almost 4 times greater than that of CIO-T2.

§5.4 Strong correlation between oxygen deficiency and Ferromagnetism

Since doped IO samples with diverse morphologies were synthesized, a comparative and systematic study will help to disclose the prevailing factors and to explicate the underlying mechanism. We further performed a comparative study on Cr:IO nanostructures involving not only NTs, but also NWs and octahedrons, aiming to gain

further understanding on the origin of the observed RTFM in Cr:IO. In addition, these nanomaterials featured with different concentrations of oxygen deficiency, which we assume may affect corresponding magnetic characteristics. Indeed, oxygen deficiency strongly correlates the FM in Cr:IO samples. As itemized in Table 1, the as-grown NW and annealed NW, the as-grown and the annealed octahedron Cr:IO samples were named as CIO-W1, CIO-W2, CIO-O1 and CIO-O2, respectively. SEM images obtained on the NW and the octahedron samples are shown in **Figures 5-5** (a) and (b). The Cr:IO NWs present with a length around 10 μm and a rectangular cross-section of 100–200 nm in dimension. The octahedron surfaces encompass 8 equilateral triangles with a side length around 200 nm. It's notable that doping Cr doesn't change the growth morphology of the products. For NWs growth, the continuous growth controlled by the 1-D growth is induced by the sufficient catalyst droplet (VLS mechanism) but the lateral growth was impeded which is resulted from relatively low In vapor generation due to decreased temperature, finally result in the formation of NWs. When switched the reagent metal source to be In powders which can generate much more In vapor even at the very low temperature then initiate the formation of octahedron growth only but constrain the 1-D growth significantly, thus the pyramid-like structure firstly and completely be structured with faceted planes to form octahedron products.

The chemical compositional and structural properties of NW and octahedron samples were investigated by XPS, XRD and Raman measurements. In **Figure 5-5** (c), the XRD results show that no detectable impurity phase was observed in the as-grown and the annealed CIO-W1, CIO-O1, CIO-W2, and CIO-O2 samples. XPS measurements were also carried out and the chemical composition formula for CIO-O1, CIO-O2, CIO-W1

and CIO-W2 can be expressed as $(\text{In}_{0.97}\text{Cr}_{0.03})_2\text{O}_{2.40}$, $(\text{In}_{0.97}\text{Cr}_{0.03})_2\text{O}_{2.80}$, $(\text{In}_{0.97}\text{Cr}_{0.03})_2\text{O}_{2.28}$ and $(\text{In}_{0.97}\text{Cr}_{0.03})_2\text{O}_{2.55}$, respectively. Thus, the Cr doping contents are the same for the NT, NW, and octahedron samples. Notably, these samples exhibit different oxygen deficiency concentrations and air annealing constantly favors to increase the oxygen content. Raman spectra [Figure 5-5 (d)] of CIO-W1, CIO-W2, CIO-O1 and CIO-O2 indicate that there are no other Raman modes related peaks due to doping of Cr.

Figure 5-5. (a) SEM image of Cr:IO NWs and (b) SEM image of octahedrons. (c) XRD patterns of CIO-W1, CIO-W2, CIO-O1 and CIO-O2, respectively. (d) Raman spectra measured on CIO-W1, CIO-W2, CIO-O1 and CIO-O2. Solid squares correspond to the Si

substrates. (e) *M-H* data of the CIO-W1 and CIO-W2 samples measured and (f) *M-H* data of CIO-O-1 and CIO-O2 obtained at 5 and 300 K.

Apparently, the magnetic characteristics of Cr:IO NWs and octahedrons are analogous to that of Cr:IO NTs. Both CIO-W1 and CIO-O1 in **Figures 5-5** (e) and (f) demonstrate clear hysteresis loops at 5 and 300 K, suggesting RTFM. As to the NW samples, the saturated magnetization at RT drops from $0.95 \mu_B/\text{Cr}$ in CIO-W1 to $0.35 \mu_B/\text{Cr}$ in CIO-W2. A similar decrease from $0.72 \mu_B/\text{Cr}$ to $0.31 \mu_B/\text{Cr}$ was detected in the octahedrons as well. Over-all, the annealed samples constantly show weakened magnetization; such tendency is also in accordance with the observed results in Cr:IO NT samples as aforementioned.

A systematic and comparative study on the as-grown and the annealed Cr:IO NT, NW and octahedron samples disclosed a close correlation between the oxygen deficiency and the FM. **Figure 5-6** shows the RT saturation magnetizations of CIO-T1, CIO-T2, CIO-W1, CIO-W2, CIO-O1, and CIO-O2 versus their corresponding concentrations of oxygen deficiency. Apparently, for this particular Cr:IO material system, the FM is boosted by the oxygen deficiency defects. Previous studies also argued that the oxygen deficiency can cause the formation of FM.¹⁸ It is notable that unlike the conventional thin film deposition, the chemical vapor transport preparation usually doesn't offer a wide-range regulation of the oxygen content during growth, and the oxygen poor ambient often leads to a severe oxygen deficiency in the as-grown products. Certainly, our results suggest that the specific synthesis strategy employed to yield Cr:IO NTs, NWs and octahedrons reliably lead to a high level of oxygen deficiency defects. As to the as-grown

and the annealed samples, the qualitative comparison among the samples is also valid and the trend revealed in **Figure 5-6** is unambiguous, even if the quantitative degrees of the oxygen deficiency may not be precisely determined by fitting the XPS data.

Figure 5-6. RT magnetizations of CIO-T1, CIO-T2, CIO-W1, CIO-W2, CIO-O1, and CIO-O2 vs. the corresponding degrees of oxygen deficiency.

The strong correlation between the oxygen deficiency and the FM must be considered aim to gain insight of the origin for observed RTFM. Since the initial idea sparked theoretical prediction and experimental discovery of DMS, there is no unified model to expatiate the experimental observations on a variety of material systems from a wide range of synthesis approaches. The inconsistencies frequently present due to extrinsic influences such as clustering formation of dopants and unintentional contaminations which could contribute to observed magnetization. Thus I took extreme care to circumvent any contamination by utilizing plastic tweezers and cross checking straws used during SQUID measurements. Pure CrO_2 phase is difficult to synthesize¹⁰⁵

thus we believe that the Cr clustering or the formation of CrO_2 cannot be responsible for the observed FM. Moreover, the XPS results in **Figure 5-2** (b) indicates that most Cr ions exhibit +3 chemical states and likely incorporate into IO matrix at the In ions lattice sites.

The conventional short range double exchange or superexchange mechanism requires high doping concentration. However, in such a low spin concentration regime, the long range ferromagnetic ordering might be established if the carrier mediated exchange interaction is effectively ferromagnetic coupled as suggested in the RKKY and the Zener models.⁴ On the other hand, the strong correlation between the oxygen deficiency and the FM in our samples implies that the formation of BMPs may dictate the magnetic ordering. A general characteristic of the BMPs model is that an essential amount of oxygen vacancies is a prerequisite to achieve the percolation threshold for the commencement of ferromagnetic ordering, which is readily fulfilled in the as-grown oxygen-deficient Cr:IO samples.

It's also noted that only the oxygen vacancies are not sufficient to establish a robust FM; the Cr dopant is indispensable. compared comparison of the $M-H$ curves of the as-grown and the annealed Cr:IO samples with those of the undoped counterparts are shown in **Figure 5-7**. The as-grown undoped NT, NW and octahedron samples are oxygen deficient too; from the obtained XPS results their nonstoichiometric formula can be determined as $\text{In}_2\text{O}_{2.57}$, $\text{In}_2\text{O}_{2.42}$ and $\text{In}_2\text{O}_{2.29}$ for IO-T1, IO-O1 and IO-W1, respectively. The oxygen-deficient undoped IO samples also show modest FM at RT, but their magnetism is more than 10 times weaker than those of the as-grown corresponding Cr:IO samples. Thus both the oxygen vacancies and the Cr doping are critical to establish stable RTFM in Indium Oxide-based DMS samples. Such observation is consistent with the

report by Hong *et al.*, who observed that the magnetic moments in IO films are much smaller than those in TiO₂ and HfO₂ films.¹³⁷ The interplay coupling between the Cr dopants and the oxygen vacancies and the potential formation of defect complex warrants further investigations.

Figure 5-7. *M-H* data taken at 300 K on (a) NT samples of CIO-O1, CIO-O2 and IO-T1; (b) NW samples of CIO-W1, CIO-W2 and IO-W1; (c) octahedron samples of CIO-O1, CIO-O2 and IO-O1.

As to the synthesized nano-Cr:IO samples, the alteration of the electronic structure caused by the Cr doping and the oxygen vacancies tends to play important roles in establishing the observed FM. A recent theoretical prediction reported that the ferromagnetic Cr-Cr interaction in Cr:IO can be adjusted and even switched through electron doping.¹²⁷ The extrinsic doping of electrons, such as the large amount of donors induced by oxygen vacancies could supply the essential carriers to stabilize the long-range ferromagnetic ordering,¹²⁷ although Cr itself may not produce any free electrons.¹²⁷ Moreover, in contrast to other semiconductors, a strong electron accumulation may occur at the IO surface,¹³⁸ which may further make the magnetic ordering surface-sensitive.

§5.5 Summary

In conclusion, a systematic study on the RTFM has been conducted on the Cr:IO nanostructures synthesized by a vapor transport technique. Extensive structural and chemical composition measurements verified the Cr doping with free cluster formation or secondary phase. A strong correlation between the enhanced FM with the oxygen deficiency in the as-grown samples was disclosed and such correlation suggests a defect-mediated mechanism; both the Cr dopants and oxygen vacancies play important and complimentary role to alter the electronic band structure of the IO host and to

stabilize the long range ferromagnetic ordering.

Chapter 6 Conclusions and Future outlook

§6.1 Summary & Conclusions

The concentration of oxygen vacancies directly regulates both the well-known defects related green emission and the FM in undoped ZnO NWs. The study not only demonstrates that undoped ZnO NWs can emit green light and show RTFM with energetic stability, but also suggests that introducing oxygen vacancies is an effective way to boost the d^0 FM. These engineered NWs with carefully tailored composition may find potential applications in nanoscale spintronic devices.

Furthermore, I have presented a report on the interface induced room-temperature FM in ZnO/Al₂O₃ core/shell structured NWs synthesized by using a vapor transport method accompanied with an atomic layer deposition technique. The sample of ZnO/Al₂O₃ core/shell NWs was further annealed in air to activate the interfacial solid-state reaction, extensive high-resolution transmission electron microscopy studies demonstrate that the ternary compound ZnAl₂O₄ was obtained in the form of adhesion shell upon the surface of ZnO core NWs. Interestingly, compared to ZnO/Al₂O₃ NWs, the enhanced FM with a magnetic signal persisting up to ~673 K was observed in sample of ZnO/ZnAl₂O₄ core/shell NWs. Our study suggests that purposely modulated interface defects in core/shell structured ZnO NWs can cause the occurrence of unpaired electrons, consequently boost the FM.

Another comparative study was carried out on typical case study of Cu-doped ZnO NWs prepared by two distinct methods and demonstrated unambiguously an enhancement of RTFM by structural inhomogeneity. Tuning the structural and the electronic

characteristics, in addition to the dopant concentration, should be an effective means to modify the ferromagnetic properties of NWs.

More in-depth studies on Cu-doped ZnO NWs investigated using transient spin-polarized optical orientation measurements were found to exhibit long-lived ($\tau_e^s > 1.5$ ns) highly spin-polarized excitonic emissions ($P_{ini} \sim 65\%$) following optical orientation under zero external B-field. These emissions originate from the acceptor-bound excitons (A^0X) – likely from the (Cu^+, h) state. This work is a proof of concept that highly spin-polarized emissions in ZnO-based materials can be achieved through doping and band structure modulation. These one-dimensional nanostructures with long-lived, highly spin polarized emissions may find potential applications as spin-polarized light emitting devices and lasers.

The RTFM has also been carried out on the Cr-doped wide-band-gap-oxide In_2O_3 nanostructures. XRD, HRTEM, Raman, and XPS measurement results confirmed the Cr doping and indicated no secondary phase or cluster formation within the detection limits. I concentrated on isolating the effect of oxygen deficiency and found a strong correlation between the enhanced FM in the as-grown samples with the essential oxygen deficiency concentrations. Such correlation suggests a defect-mediated mechanism; both the Cr dopants and the oxygen vacancies play critical and complimentary role to alter the electronic band structure of the IO host and to stabilize the long-range ferromagnetic ordering.

§6.2 Recommendations for future works

The studies presented in this thesis are mainly focused on the investigation of

ferromagnetic wide-band-gap oxides, ZnO and In_2O_3 based DMOs. Although comprehensive studies have been carried out to understand its physical origin of FM, but few works have been carried out on the spin-polarized transport, like in homojunction made from doped-ZnO/ In_2O_3 . Recent reports demonstrate that progress is far from dormant. This is very demanding, because they not only have impact on application of DMOs but also provide information for spin injection. The spin injection, transportation and detection from doping ZnO layer to pure ZnO and other conventional semiconductors is an important long-term goal of the continuing of ZnO DMOs.¹²⁻¹⁶ Clearly, there is a pressing need for spin-based devices consisted with high T_c and P_s DMOs to enhance the operation temperature and elevate spin injection efficiency then eventually to achieve RT device paradigms.

The demonstration of ZnO based spin-valve (SV) is an essential extension of this presented dissertation, suggest an interesting research direction. It is highly desirable to design and fabricate high quality epitaxial thin films and NWs of strategically important spintronic wide-band-gap oxide materials. The key to constructing high performance devices, in particular, SV based on the doped oxides, we propose to build up ZnO-based homojunction with magnetically defined components to solve the potential conductivity mismatching and notorious low spin injection issues. Simultaneously to investigate the dynamics of charges and spins, including the charge transfer process, spin polarization degree, spin relaxation lifetime and dephasing length in the spintronic wide-band-gap oxides based devices.

In this proposed future research, several prominent advantages over the conventional geometry are envisioned:

- (i) with fully epitaxial heterostructures, photolithography can be easily applied to define the device structures;
- (ii) spin injection of polarized carriers probed by *optical orientation* (or measuring magnetoresistance of spin-injection device) experiments from the ferromagnetic source through the fully epitaxial interface may give a high efficiency;
- (iii) waveguide-like transport may be realized in such well-defined structure, leading to more effective spin modulation;
- (iv) heating effect will be dramatically reduced since spintronic devices are based on spin manipulation and consume much less power.

Figure 6-1. Schematic representation of (Cu:ZnO)/Al:ZnO/(Nd:ZnO) spin valve.

The SV is the simplest magnetoresistive device. It consists of two ferromagnetic layers separated by a metallic/conductive spacer, one of which is free to switch between parallel and antiparallel alignments corresponding to the low and high resistivity states, respectively. As shown in **Figure 6-1**, two ferromagnetic layers with different coercivity values separated by a conductive spacer Al:ZnO, this sandwich structure is defined by

side insulators and contact with top/down Al:ZnO layers. The good lattice matching between Al:ZnO and sapphire warrants the fully epitaxial growth as reported by Jun Hong Noh, *et al.*,¹³⁹ e.g. in **Figure 6-1**. And highly conductive Al-doped ZnO is the most widely used transparent conductive oxide, which may offer further magneto-optical applications. In addition, the well-established Ohmic contact between the Al/Pt and Al:ZnO helps to ensure the experimental feasibility.¹⁴⁰

One important feature of this proposed structure is that it consists of two ferromagnetic layers with different coercivity values [e.g. $H_c((\text{Zn,Nd})\text{O}) > H_c((\text{Zn,Cu})\text{O})$], which was also confirmed by our preliminary experimental results. (Zn,Nd)O with higher H_c could be used to pin the magnetic orientation of one layer and the other layer is tuned by the applied external magnetic field. Such an all ZnO SV will be very unique and we have developed all the essential elements in our lab for its construction. In the devices, since the CuZnO ferromagnetic semiconductor layers touched the ZnO space layer directly, the significant spin injection from CuZnO into ZnO was observed by measuring the magnetoresistance of the spin-injection devices.

So this project will be quite feasible. However we still need to confront with some challenges involving the contact resistance mismatch, limited spin lifetime, uncertain spin-orbital coupling and so on. But I'm confident that this proposed future projects could be started and use such unique structures to achieve some insights.

Bibliography

1. S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova and D. M. Treger, *Science* **294** (5546), 1488-1495 (2001).
2. T. Dietl, H. Ohno, F. Matsukura, J. Cibert and D. Ferrand, *Science* **287**, 1019-1022 (2000).
3. C. Jagadish and S. J. Pearton, *Zinc oxide bulk, thin films and nanostructures: processing, properties and applications*. (Elsevier Science Ltd, 2006).
4. C. Klingshirn, *Chemphyschem* **8** (6), 782-803 (2007).
5. A. B. Djurišić and Y. H. Leung, *Small* **2** (8-9), 944-961 (2006).
6. T. Fukumura, Z. Jin, A. Ohtomo, H. Koinuma and M. Kawasaki, *Applied Physics Letters* **75**, 3366 (1999).
7. W. J. Fan, J. B. Xia, P. A. Agus, S. T. Tan, S. F. Yu and X. W. Sun, *Journal of Applied Physics* **99**, 013702 (2006).
8. Ü Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho and H. Morko, *Journal of Applied Physics* **98**, 041301 (2005).
9. K. L. Chopra, S. Major and D. K. Pandya, *Thin Solid Films* **102** (1), 1-46 (1983).
10. H. L. Hartnagel, A. L. Dawar, A. K. Jain, C. Jagadish and S. J. Pearton, *Semiconducting transparent thin films*. (Institute of Physics Pub., 1995).
11. J. Philip, A. Punnoose, B. I. Kim, K. M. Reddy, S. Layne, J. O. Holmes, B. Satpati, P. R. Leclair, T. S. Santos and J. S. Moodera, *Nat. Mater* **5**, 298 (2006).
12. T. Fukumura, H. Toyosaki and Y. Yamada, *Semiconductor Science and*

- Technology **20**, S103 (2005).
13. D. C. Kundaliya, S. B. Ogale, S. E. Lofland, S. Dhar, C. J. Metting, S. R. Shinde, Z. Ma, B. Varughese, K. V. Ramanujachary and L. Salamanca-Riba, Nature materials **3** (10), 709-714 (2004).
 14. J. R. Neal, A. J. Behan, R. M. Ibrahim, H. J. Blythe, M. Ziese, A. M. Fox and G. A. Gehring, Physical review letters **96** (19), 197208 (2006).
 15. X. H. Xu, H. J. Blythe, M. Ziese, A. J. Behan, J. R. Neal, A. Mokhtari, R. M. Ibrahim, A. M. Fox and G. A. Gehring, New Journal of Physics **8**, 135 (2006).
 16. S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova and D. M. Treger, Science **294**, 1488 (2001).
 17. T. Dietl, D. D. Awschalom, M. Kaminska and H. Ohno, Spintronics Elsevier: Oxford, 2008.
 18. S. D. Bader, Surface Science **500** (1-3), 172-188 (2002).
 19. C. M. Lieber, Mrs Bulletin **28** (7), 486-491 (2003).
 20. M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo and P. Yang, Science **292** (5523), 1897-1899 (2001).
 21. G. Z. Xing, J. B. Yi, J. G. Tao, T. Liu, L. M. Wong, Z. Zhang, G. P. Li, S. J. Wang, J. Ding, T. C. Sum, C. H. A. Huan and T. Wu, Adv. Mater. **20** (18), 3521-3527 (2008).
 22. G. Z. Xing, D. D. Wang, J. B. Yi, L. L. Yang, M. Gao, M. He, J. H. Yang, J. Ding, T. C. Sum and T. Wu, Applied Physics Letters **96**, 112511 (2010).
 23. G. Z. Xing, J. B. Yi, D. D. Wang, L. Liao, T. Yu, Z. X. Shen, C. H. A. Huan, T. C. Sum, J. Ding and T. Wu, Physics Review B **79**, 174406 (2009).

24. Y. Li, G. S. Cheng and L. D. Zhang, Journal of Materials Research **15** (11), 2305-2308 (2000).
25. B. B. Lakshmi, C. J. Patrissi and C. R. Martin, Chem. Mater **9** (11), 2544-2550 (1997).
26. Z. Miao, D. Xu, J. Ouyang, G. Guo, X. Zhao and Y. Tang, Nano Letters **2** (7), 717-720 (2002).
27. Z. Li, Y. Xiong and Y. Xie, Inorg. Chem **42** (24), 8105-8109 (2003).
28. H. Zhang, D. Yang, Y. Ji, X. Ma, J. Xu and D. Que, J. Phys. Chem. B **108** (13), 3955-3958 (2004).
29. B. Liu and H. Zeng, Langmuir **20** (10), 4196-4204 (2004).
30. B. Cheng and E. Samulski, Chemical communications **2004** (8), 986-987 (2004).
31. Z. Y. Fan and J. G. Lu, Journal of nanoscience and nanotechnology **5** (10), 1561-1573 (2005).
32. P. D. Yang, H. Q. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. R. He and H. J. Choi, Adv. Funct. Mater. **12** (5), 323-331 (2002).
33. Z. L. Wang, J. Phys.: Condens. Matter **16**, 829-858 (2004).
34. G. Z. Xing, X. S. Fang, Z. Zhang, D. D. Wang, X. Huang, J. Guo, L. Liao, Z. Zheng, H. R. Xu and T. Yu, Nanotechnology **21**, 255701 (2010).
35. <http://www.nanoscience.gatech.edu/zlwang/research/pvd.html>.
36. R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. **4** (5), 89-90 (1964).
37. V. Aleskovskii and Z. P. Khim, J. Appl. Chem. USSR. **47** (10), 2207 (1974).
38. R. L. Puurunen, J. Appl. Phys. **97**, 121301 (2005).
39. A. A. Malygin, J. Ind. Eng. Chem. **12** (1), 1 (2006).

40. http://ald.colorado.edu/J_Phys_Chem_100.pdf
41. D. Moore and R. Reynolds, X-ray Diffraction and the Identification and Analysis of Clay Minerals. (Oxford University Press Oxford, 1989).
42. N. Colthup, L. Daly and S. Wiberley, Introduction to infrared and Raman spectroscopy. (Academic press New York, 1990).
43. R. Stöckle, Y. Suh, V. Deckert and R. Zenobi, Chemical Physics Letters **318** (1-3), 131-136 (2000).
44. C. Oatley, W. Nixon and R. Pease, Advances in Electronics and Electron Physics **21**, 181-247 (1966).
45. A. Crewe, J. Wall and L. Welter, Journal of Applied Physics **39** (13), 5861-5868 (2009).
46. D. Williams and C. Carter, Transmission Electron Microscopy, 3-22 (2009).
47. R. Van Grieken and A. Markowicz, (1993).
48. J. Goldstein, D. Newbury, D. Joy, P. Echlin, C. Lyman and E. Lifshin, Scanning electron microscopy and X-ray microanalysis. (Springer Us, 2003).
49. R. Carlton, C. Lyman and J. Roberts, Scanning **26** (4), 167-174 (2004).
50. J. Hollander and W. Jolly, Accounts of Chemical Research **3** (6), 193-200 (1970).
51. J. Moulder, W. Stickle, P. Sobol and K. Bomben, Perkin-Elmer: Boca Raton, FL (1992).
52. K. Wanner and G. Höfner, Mass spectrometry in medicinal chemistry. (Wiley-VCH, 2007).
53. R. Kaufmann, B. Spengler and F. Lützenkirchen, Rapid Communications in Mass Spectrometry **7** (10), 902-910 (1993).

54. G. Binnig, C. Quate and C. Gerber, Physical review letters **56** (9), 930-933 (1986).
55. U. Hartmann, Annual Review of Materials Science **29** (1), 53-87 (1999).
56. L. Abelman, S. Porthun, M. Haast, C. Lodder, A. Moser, M. Best, P. van Schendel, B. Stiefel, H. Hug and G. Heydon, Journal of Magnetism and Magnetic Materials **190** (1-2), 135-147 (1998).
57. J. Lakowicz and B. Masters, Journal of Biomedical Optics **13**, 029901 (2008).
58. H. Nalwa and L. Rohwer, (2003).
59. S. Studenikin and M. Cocivera, Journal of Applied Physics **91**, 5060 (2002).
60. J. Stathis and M. Kastner, Physical Review B **35** (6), 2972-2979 (1987).
61. L. Lewis and K. Bussmann, Review of Scientific Instruments **67** (10), 3537-3542 (2009).
62. D. Drung, C. Assmann, J. Beyer, A. Kirste, M. Peters, F. Ruede and T. Schurig, Applied Superconductivity, IEEE Transactions on **17** (2), 699-704 (2007).
63. K. Ando, H. Saito, Z. Jin, T. Fukumura, M. Kawasaki, Y. Matsumoto and H. Koinuma, Journal of Applied Physics **89**, 7284 (2001).
64. A. Walsh, J. L. F. Da Silva and S. H. Wei, Physical review letters **100** (25), 256401 (2008).
65. A. Sundaresan, R. Bhargavi, N. Rangarajan, U. Siddesh and C. N. R. Rao, Physical Review B **74** (16), 161306 (2006).
66. S. B. Ogale, Adv. Mater. **22**, 3125 (2010).
67. M. A. Garcia, J. M. Merino, E. F. Pinel, A. Quesada, J. d. I. Venta, M. L. R. Gonzalez, G. R. Castro, P. Crespo, J. Llopis, J. M. Gonzalez-Calbet and A. Hernando, Nano Lett. **7**, 1489 (2007).

68. Ü. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho and H. Morko, J. Appl. Phys. **98**, 041301 (2005).
69. Y. Yang, R. Scholz, A. Berger, D. Kim, M. Knez, D. Hesse, U. Gösele and M. Zacharias, Small **4** (12), 2112-2117 (2008).
70. Y. Yang, D. Kim, M. Knez, R. Scholz, A. Berger, E. Pippel, D. Hesse, U. Gosele and M. Zacharias, J. Phys. Chem. C **112**, 4068 (2008).
71. M. Venkatesan, C. B. Fitzgerald and J. M. D. Coey, Nature **430** (7000), 630-630 (2004).
72. N. H. Hong, J. Sakai, N. Poirot and V. Brizé, Physical Review B **73** (13), 132404 (2006).
73. Y. W. Ma, J. Ding, D. C. Qi, J. B. Yi, H. M. Fan, H. Gong, A. T. Wee and A. Rusydi, Applied Physics Letters **95**, 072501 (2009).
74. S. Banerjee, M. Mandal, N. Gayathri and M. Sardar, Appl. Phys. Lett. **91**, 182501 (2007).
75. Y. Yang, R. Scholz, A. Berger, D. S. Kim, M. Knez, D. Hesse, U. Gösele and M. Zacharias, Small **4** (12), 2112-2117 (2008).
76. I. S. Elfimov, S. Yunoki and G. A. Sawatzky, Physical review letters **89** (21), 216403 (2002).
77. J. M. D. Coey, Solid State Sciences **7** (6), 660-667 (2005).
78. A. L. Schoenhalz, J. T. Arantes, A. Fazzio and G. M. Dalpian, Applied Physics Letters **94**, 162503 (2009).
79. A. Sundaresan and C. N. R. Rao, NanoToday **4** (1), 96-106 (2009).
80. S. B. Ogale, Advanced Materials **22**, 3125 (2010).

81. J. M. Coey, M. Venkatesan and C. B. Fitzgerald, *Nat. Mater.* **4**, 173-179 (2005).
82. K. Klier, *Advances in Catalysis* **31**, 243-313 (1982).
83. L. H. Ye, A. J. Freeman and B. Delley, *Physical Review B* **73** (3), 33203 (2006).
84. M. S. Park and B. I. Min, *Physical Review B* **68** (22), 224436 (2003).
85. R. Q. Wu, G. W. Peng, L. Liu, Y. P. Feng, Z. G. Huang and Q. Y. Wu, *Applied Physics Letters* **89**, 062505 (2006).
86. K. Ando, H. Saito, Z. W. Jin, T. Fukumura, M. Kawasaki, Y. Matsumoto and H. Koinuma, *Journal of Applied Physics* **89** (11), 7284 (2001).
87. D. J. Keavney, D. B. Buchholz, Q. Ma and R. P. H. Chang, *Appl. Phys. Lett.* **91**, 012501 (2007).
88. Z. L. Wang, *J. Phys.: Condens. Matter* **16**, R829 (2004).
89. M. H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber and P. Yang, *Adv. Mater.* **13**, 113 (2001).
90. D. Chakraborti, J. Narayan and J. T. Prater, *Appl. Phys. Lett.* **90**, 062504 (2007).
91. X. Wang, J. B. Xu, W. Y. Cheung, J. An and N. Ke, *Applied Physics Letters* **90**, 212502 (2007).
92. J. W. Chai, J. S. Pan, S. J. Wang, C. H. A. Huan, J. S. Chen and S. Xu, *Applied Physics Letters* **86**, 222505 (2005).
93. A. C. Mofor, A. El-Shaer, A. Bakin, A. Waag, H. Ahlers, U. Siegner, S. Sievers, M. Albrecht, W. Schoch, N. Izyumskaya, V. Avrutin, S. Sorokin, S. Ivanov and J. Stoimenos, *Appl. Phys. Lett.* **87** (6), 062501 (2005).
94. D. B. Buchholz, R. P. H. Chang, J. H. Song and J. B. Ketterson, *Appl. Phys. Lett.* **87**, 082504 (2005).

95. D. L. Hou, X. J. Ye, H. J. Meng, H. J. Zhou, X. L. Li, C. M. Zhen and G. D. Tang, Appl. Phys. Lett. **90**, 142502 (2007).
96. J. L. MacManus-Driscoll, N. Khare, Y. Liu and M. E. Vickers, Adv. Mater. **19**, 2925 (2007).
97. W. H. Brumage, C. F. Dorman and C. R. Quade, Phys. Rev. B **63**, 104411 (2001).
98. Y. Xin, J. Lu, P. A. Stampe and R. J. Kennedy, Appl. Phys. Lett. **88**, 112512 (2006).
99. L.-H. Ye, A. J. Freeman and B. Delley, Phys. Rev. B **73**, 033203 (2006).
100. T. Dubroca, J. Hack and R. Hummel, Phys. Rev. B **74**, 026403 (2006).
101. T. C. Kaspar, S. M. Heald, C. M. Wang, J. D. Bryan, T. Droubay, V. Shutthanandan, S. Thevuthasan, D. E. McCready, A. J. Kellock, D. R. Gamelin and S. A. Chambers, Phys. Rev. Lett. **95**, 217203 (2005).
102. T. S. Herng, S. P. Lau, S. F. Yu, H. Y. Yang, X. H. Ji, J. S. Chen, N. Yasui and H. Inaba, Journal of Applied Physics **99**, 086101 (2006).
103. P. V. Radovanovic and D. R. Gamelin, Phys. Rev. Lett. **91**, 157202 (2003).
104. A. C. Durst, R. N. Bhatt and P. A. Wolff, Phys. Rev. B **65** (23), 235205 (2002).
105. A. Kaminski and S. Das Sarma, Phys. Rev. Lett. **88** (24), 247202 (2002).
106. S. Ghosh, V. Sih, W. H. Lau, D. D. Awschalom, S. Y. Bae, S. Wang, S. Vaidya and G. Chapline, Applied Physics Letters **86**, 232507 (2005).
107. D. Lagarde, A. Balocchi, P. Renucci, H. Carrère, F. Zhao, T. Amand, X. Marie, Z. X. Mei, X. L. Du and Q. K. Xue, Physical Review B **78** (3), 33203 (2008).
108. D. Lagarde, A. Balocchi, P. Renucci, H. Carrère, T. Amand, X. Marie, Z. X. Mei and X. L. Du, Physical Review B **79** (4), 45204 (2009).

109. W. M. Chen, I. A. Buyanova, A. Murayama, T. Furuta, Y. Oka, D. P. Norton, S. J. Pearton, A. Osinsky and J. W. Dong, Applied Physics Letters **92**, 092103 (2008).
110. S. J. Pearton, D. P. Norton, M. P. Ivill, A. F. Hebard, J. M. Zavada, W. M. Chen and I. A. Buyanova, Journal of Electronic Materials **36** (4), 462-471 (2007).
111. D. C. Reynolds, D. C. Look, B. Jogai, C. Litton, G. Cantwell and W. C. Harsch, Physical Review B **60** (4), 2340-2344 (1999).
112. L. M. Huang, A. L. Rosa and R. Ahuja, Physical Review B **74** (7), 75206 (2006).
113. Z. H. Xiong, S. Q. Shi, Q. X. Wan and F. Y. Jiang, Physica Scripta **2007**, 358 (2007).
114. W. R. L. Lambrecht, A. V. Rodina, S. Limpijumnong, B. Segall and B. K. Meyer, Physical Review B **65** (7), 75207 (2002).
115. B. Gil, Physical Review B **64** (20), 201310 (2001).
116. J. R. Haynes, Physical review letters **17** (16), 860-862 (1966).
117. I. Broser, L. Podlowski, P. Thurian, R. Heitz and A. Hoffmann, Journal of Luminescence **60&61**, 588-591 (1994).
118. N. H. Hong, J. Sakai, N. T. Huong and V. Briz, Appl. Phys. Lett. **87**, 102505 (2005).
119. N. H. Hong, J. Sakai, N. T. Huong, A. Ruyter and V. Briz, J. Phys.: Condens. Matter **18**, 6897-6905 (2006).
120. G. Peleckis, X. L. Wang and S. X. Dou, Appl. Phys. Lett. **88**, 132507 (2006).
121. S. J. Hu, S. S. Yan, X. L. Lin, X. X. Yao, Y. X. Chen, G. L. Liu and L. M. Mei, Applied Physics Letters **91** (26) (2007).
122. D. W. Chu, Y. P. Zeng and D. L. Jiang, Applied Physics Letters **92**, 182507 (2008).

123. J. Philip, A. Punnoose, B. I. Kim, K. M. Reddy, S. Layne, J. O. Holmes, B. Satpati, P. R. Leclair, T. S. Santos and J. S. Moodera, *Nature materials* **5** (4), 298-304 (2006).
124. P. Kharel, C. Sudakar, M. B. Sahana, G. Lawes, R. Suryanarayanan, R. Naik and V. M. Naik, *Journal of Applied Physics* **101** (9), 09H117 (2009).
125. L. Bizo, M. Allix, H. Niu and M. J. Rosseinsky, *Advanced Functional Materials* **18** (5), 777-784 (2008).
126. P. F. Xing, Y. X. Chen, S. S. Yan, G. L. Liu, L. M. Mei, K. Wang, X. D. Han and Z. Zhang, *Applied Physics Letters* **92** (2), 022513 (2009).
127. H. Raebiger, S. Lany and A. Zunger, *Physical review letters* **101** (2), 027203 (2008).
128. H. J. Fan, R. Scholz, M. Zacharias, U. Gösele, F. Bertram, D. Forster and J. Christen, *Appl. Phys. Lett* **86**, 023113 (2005).
129. J. B. Hannon, S. Kodambaka, F. M. Ross and R. M. Tromp, *Nature* **440**, 69-71 (2006).
130. Y. G. Yan, Y. Zhang, H. B. Zeng and L. D. Zhang, *Crystal Growth & Design* **7**, 941-943 (2007).
131. R. D. Shannon and C. T. Prewitt, *Structural Crystallography and Crystal Chemistry* **25**, 925-946 (1969).
132. N. J. C. Ingle, R. H. Hammond and M. R. Beasley, *J. Appl. Phys.* **89**, 4631-4635 (2001).
133. M. S. Lee, W. C. Choi, E. K. Kim, C. K. Kim and S. K. Min, *Thin Solid Films* **279**, 1-3 (1996).

134. S. Lany and A. Zunger, Physical review letters **98** (4), 045501 (2007).
135. H. Q. Cao, X. Q. Qiu, Y. Liang, Q. M. Zhu and M. J. Zhao, Appl. Phys. Lett **83**, 761-763 (2003).
136. Y. F. Hao, G. W. Meng, C. H. Ye and L. D. Zhang, Cryst. Growth Des **5**, 1617–1621 (2005).
137. A. Walsh, J. L. F. Da Silva, S. H. Wei, C. Körber, A. Klein, L. F. J. Piper, A. DeMasi, K. E. Smith, G. Panaccione and P. Torelli, Physical review letters **100** (16), 167402 (2008).
138. S. Kuroda, N. Nishizawa, K. Takita, M. Mitome, Y. Bando, K. Osuch and T. Dietl, Nature materials **6** (6), 440-446 (2007).
139. J. H. Noh, I. S. Cho, S. Lee, C. M. Cho, H. S. Han, J. S. An, C. H. Kwak, J. Y. Kim, H. S. Jung and J. K. Lee, physica status solidi (a) **206** (9), 2133-2138 (2009).
140. H. Kim, I. Adesida, K. Kim, S. Park and T. Seong, Journal of The Electrochemical Society **151**, G223 (2004).