Metal oxide nanostructures and their field emission properties

Zheng, Zhe

2010

Zheng, Z. (2010). Metal oxide nanostructures and their field emission properties. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/47511>

<https://doi.org/10.32657/10356/47511>

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**Metal oxide nanostructures and their field
emission properties**

Zheng Zhe

(B. Sc., Fudan University, P. R. China)

School of Physical and Mathematical Sciences

A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
Doctor of Philosophy of Physics

2010

Abstract

ABSTRACT

This thesis presents shape controlled synthesis of iron (Fe) and tungsten (W) oxides nanostructures and their field induced electron emission (FE) properties.

The Hot-Plate growth method, also called Heat-Oxide growth method, was adapted to grow randomly aligned α -Fe₂O₃ and potassium tungsten bronze (PTB) nanostructures at different temperatures. This Heat-Oxide method provides an alternative route for fabrication of metal oxide nanostructures, with the advantages of mild synthetic conditions and scalability for large-scale production.

Particularly, ultra-sharp α -Fe₂O₃ nanoflakes were synthesized at 260 °C, which is the lowest growth temperature reported in the literature. A series of characterization, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and micro-Raman spectroscopy, were used to identify the morphology and crystal structures of these nanoflakes. Their growth mechanisms were also systemically studied. The results from TEM and SEM observations revealed that the direct growth of α -Fe₂O₃ nanoflakes was governed by surface diffusion mechanism. Furthermore, these ultra-sharp nanoflakes exhibit a low emission turn-on field of 7.2 V/ μ m and high emission current density 12 μ A/cm² in large area FE processes. In addition, Argon plasma treatment was employed to remove amorphous layers and create sub-tips on the surface of these nanoflakes. Such tips are believed to contribute to the enhancement of emission.

The Heat-Oxide method was also used to fabricate tungsten oxide nanostructures with simple and direct potassium doping. The growth mechanisms of these nanostructures were different from that of α -Fe₂O₃ nanoflakes. SEM observations of a series of samples grown for different duration show that the formations of PTB nanowire and nanosheets are *via* Vapor-Solid mechanisms. Polarization dependent Raman study and electrical transport properties of individual PTB nanowires were also investigated. Anisotropic crystal structures and metallic property were found in

Abstract

these nanowires. Finally, the FE properties of individual PTB nanowires were studied by controllably altering anode shapes, electrodes spacing and alignment of the two electrodes. Remarkably, extra gate electric field was introduced into FE process of individual nanowire according to triode-type FE setup. All experimental results were supported by finite element simulations.

Acknowledgements

ACKNOWLEDGEMENTS

I would like to express my earnest thankfulness to many people for their guidance, support and friendship.

In particular, great gratitude should be extended to my supervisor, Asst. Prof. Yu Ting. The completion of this thesis would unlikely be successful without his patience and instruction in many ways. His invaluable advice and experience are of great benefit not only to the research, but also to the attitude towards my future life.

I am grateful to my co-supervisor, Prof. Shen ZeXiang for his continuous guidance and support through my entire Ph. D study.

I would also like to thank following persons who helped me in one way or another.

Dr. Chen Yunzhong, and Dr. Zhang Jingxuan for their help with the TEM and EDS characterization; Dr. You Yumeng, Dr. Ni Zhenhua and Mr. Yan Bin, for their assistance in analysis of polarized Raman images and spectra; Dr. Du Chaoling and Miss Wong Choun Pei, for their help in simulation; Dr. Ma Yun, for her help of PLD deposition; Dr. Wang Haomin for his help of general data analysis and results discussion.

I would also like to express my sincere thanks to members in our group. Their supports are not only in the valuable discussion of research work, but also for their friendship and the happy time spent together. I am also grateful to all research scholars in SMPS PAP for sharing their experiences of living and studying with me.

On a personal note, I wish to express my heartfelt appreciation to my parents for their continuous support and blessings during my purchasing a higher degree process.

Table of Contents

TABLE OF CONTENTS

ABSTRACT	i
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	iv
LIST OF FIGURES	vii
LIST OF TABLES	xiii
LIST OF SYMBOLS	xiv
CHAPTER I: Introduction	1
1.1 Background.....	1
1.2 Metal oxide nanostructures.....	2
1.2.1 Classification of metal oxide nanostructures.....	3
1.2.2 One-dimensional metal oxide nanostructures.....	4
1.2.3 Growth of one-dimensional metal oxide nanostructures.....	10
1.2.4 Modification of one-dimensional metal oxide nanostructures.....	16
1.2.5 Applications of one-dimensional metal oxide nanostructures.....	20
1.3 Field electron emission.....	24
1.3.1 Electron emission mechanisms.....	24
1.3.2 Surface potential barrier.....	26
1.3.3 Fowler–Nordheim (<i>F-N</i>) tunneling.....	29
1.3.4 Field emission in one-dimensional metal oxide nanostructures.....	35
1.4 Motivation and objectives.....	38
1.5 Organization of this thesis.....	41
CHAPTER II: Experimental details	43
2.1 Sample preparation and device fabrication.....	43
2.1.1 Sample preparation.....	43
2.1.2 Device fabrication.....	44

Table of Contents

2.2 Electrical transport measurement setup.....	45
2.3 Reactive Ion Etching (RIE) and plasma bombardment treatment.....	46
2.4 Field emission experimental setup.....	48
2.4.1 Field emission setup for nanostructured film.....	48
2.4.2 Field emission setup for individual nanowire.....	49

CHAPTER III: Synthesis and characterization of α -Fe₂O₃ nanoflake and their field emission properties

3.1 Introduction.....	53
3.2 Morphology and crystal structure.....	53
3.3 Growth mechanism of α -Fe ₂ O ₃ nanoflakes.....	57
3.4 Field emission from α -Fe ₂ O ₃ nanoflake films.....	59
3.5 Plasma bombardment treated α -Fe ₂ O ₃ nanoflakes.....	61
3.5.1 Modification of crystal structure.....	62
3.5.2 Field emission enhancement.....	65
3.6 Summary.....	67

CHAPTER IV: Growth and characterization of potassium tungsten bronze nanostructures and their field emission properties

4.1 Introduction.....	69
4.2 Morphology and crystal structure.....	69
4.3 Growth mechanism of potassium tungsten bronze (PTB) nanostructures.....	74
4.3.1 Growth mechanism of PTB nanowire.....	75
4.3.2 Growth mechanism of PTB nanosheet.....	76
4.4 Electrical transport in individual nanowire device.....	78
4.5 Polarized micro-Raman scattering of individual nanowire.....	79
4.6 Field emission from nanowire films.....	83
4.7 Summary.....	84

Table of Contents

CHAPTER V: Field emission properties of individual potassium tungsten bronze nanowire **86**

5.1 Introduction..... 86

5.2 Anode shape influence.....87

 5.2.1 Experimental results and discussion.....87

 5.2.2 Simulation results and analysis..... 91

5.3 Electrodes off-axis influence..... 92

5.4 Side gate effect.....94

 5.4.1 Experimental results and discussion.....94

 5.4.2 Simulation results and analysis..... 97

5.5 Summary.....99

CHAPTER VI: Conclusions **101**

REFERENCES **104**

LIST OF PUBLICATIONS **117**

List of Figures

LIST OF FIGURES

Figure 1.1 Crystal structure model of α -Fe₂O₃ viewed in [110] direction.....5

Figure 1.2 Typical scanning electron microscopy (SEM) image of α -Fe₂O₃ nanoflakes on an atomic force microscopy (AFM) tip. Inset shows a high magnification SEM image of the tip apex..... 7

Figure 1.3 The structural motif of the arrangement of WO₆ octahedral in the (a) cubic (b) orthorhombic and (c) hexagonal phases of tungsten trioxide..... 8

Figure 1.4 The diagram of cross-section view in the *ab* plane perpendicular to the *c* axis when the potassium ions (blue ball) occupy the hexagonal WO₆ octahedral (yellow tetragon) channels. The structure is filled at *x* = 0.33..... 9

Figure 1.5 A schematic diagram of experimental apparatus that is used in vapor phase growth methods including chemical vapor deposition (CVD), thermal evaporation, and pulsed laser deposition (PLD)..... 11

Figure 1.6 (a-c) Optical images of the pure iron foil (10 cm × 10 cm) a) before heating, b, c) after heating at 300 °C for 10 min and 24 h, respectively. (d-f) Corresponding SEM images of foil surfaces shown in (a-c). The size of the α -Fe₂O₃ nanoflake gradually increase with the heating duration increases..... 12

Figure 1.7 The proposed 1D metal oxide nanostructure growth model. (a) The liquid metal alloy droplet formation and the O₂ in the inlet flow absorbed and reacted to the alloy. (b) Liquid metal oxide supersaturated and precipitated nanoclusters which serve as nuclei. (c) The growth of 1D metal oxide nanostructure continues along one particular crystallographic orientation. (d) Growth terminates when the source metal is exhausted.....15

Figure 1.8 (a) Current vs. voltage (*I-V*) curves of the *p*-type α -Fe₂O₃ nanobelt devices doped with Zn source at 700 °C (inset is current vs. gate voltage (*I-V_g*) curve). (b) *I-V* curves of the enhanced *n*-type α -Fe₂O₃ nanobelt devices doped with Zn source at 350 °C (inset is *I-V_g* curve).....17

List of Figures

Figure 1.9 (a) Transmission electron microscopy (TEM) image of an as-grown CuO nanowire. The inset shows a high resolution TEM (HRTEM) image from the tip part. (b) TEM image of a CuO nanowire after exposure to 10 min of O ₂ plasma. Insets are the HRTEM images of different parts. (c) TEM image of a CuO nanowire after 10 min of CF ₄ plasma.....	18
Figure 1.10 (a) Typical field emission (FE) current density vs. electrical field (J - E) curves and Fowler-Nordheim (F - N) plots (inset) of as-grown and O ₂ plasma-treated CuO nanowires. (b) Typical FE J - E curves and F - N plots (inset) of as-grown and CF ₄ plasma-treated CuO nanowires.....	19
Figure 1.11 Typical FE J - E curves of CuO nanowires with H ₂ plasma treatment; untreated, treated for 5, 10 and 15 min.....	20
Figure 1.12 (a) A schematic diagram of experimental setup testing a nanobelt field effect transistor (FET). (b) Current vs. source-drain voltage (I - V_{ds}) characteristics of α -Fe ₂ O ₃ nanobelt FET obtained at back gate potentials of -10 V, 0 V, and 10 V. Bottom inset: Energy band diagram of Ni-Fe ₂ O ₃ nanobelt contact, ϕ is the work function. Top inset: I - V_g curve of the nanobelt FET obtained at 2.0 V source-drain bias.....	22
Figure 1.13 Emission spectra from ZnO nanowire arrays below (a) and above ((b) and inset)) the lasing threshold, respectively. The pump powers for these spectra are 20, 100, and 150 kW/cm ² , respectively.	23
Figure 1.14 Electron emission classifications based on emission mechanisms.....	24
Figure 1.15 Schematic diagram of one-dimension potential well with flat bottom.....	27
Figure 1.16 Schematic diagrams of the potential barriers on the interface between the electron emitting surface and vacuum at (a) zero and (b) strong external applied field.	31
Figure 1.17 Schematic illustration of evaluating indicator in FE process.....	33
Figure 1.18 The progress road map of FE study on metal oxide nanostructures.....	36
Figure 1.19 (a) Setup of the <i>in situ</i> measurement. (b) A single pure ZnO nanowire with a diameter of approximately 100 nm and (c) In-doped ZnO nanowire with a diameter of approximately 100 nm used in FE measurement.....	41

List of Figures

Figure 1.20 (a) I - V curves and (b) the corresponding F - N plots for a single In-doped ZnO nanowire and pure one, respectively. The lines in the F - N plots are the linear fit of the experimental curves.....	42
Figure 2.1 (a) Schematic diagram of a single potassium tungsten bronze (PTB) nanowire FET configuration with basic electrical setup. (b) Optical image of the FET.	45
Figure 2.2 (a) Keithley 4200 SCS (semiconductor characterization system). (b) Suss probe station.....	46
Figure 2.3 A schematic diagram of reactive ion etching (RIE) system.....	47
Figure 2.4 Schematic of film sample FE test system setup.....	49
Figure 2.5 (a) Optical image of the tungsten (W) tip into the suspension droplet on CNT film. (b) Illustration of the setup for attachment of PTB nanowires to an etched W tip using the dielectrophoresis effect. (c) SEM image of an individual PTB nanowire attached to the electrochemically etched W tip.....	50
Figure 2.6 FE measurement apparatus and parameters. (a) Optical image of the experimental setup in SEM chamber. (b) The SEM image with schematic diagram of the experimental setup. The inset image shows the nanowire of the length l and diameter w with the sharp anode positioned at a distance d and the single-side-gate positioned at a distance d'	51
Figure 2.7 (a) and (b) SEM images showing typical experimental configuration and definition of distance d between two electrodes with flat plane anode setup and tip anode setup, respectively. (c) SEM image showing typical experimental configuration and definition of the angle α between two electrodes with tip anode setup.....	52
Figure 3.1 SEM images of the top surfaces of Fe foils heated for 10 hours at (a) 260 °C, (b) 300 °C, (c) 350 °C and (d) 400 °C.....	54
Figure 3.2 (a) (a1 - a4) High magnification SEM images of the nanoflakes synthesized at 260, 300, 350, and 400 °C, respectively. (b) Aspect ratio (solid squares) defined as length over full width at half length and radii (solid circles) of tangent circles of the tips as a function of heating temperatures.....	55
Figure 3.3 (a) X-ray diffraction (XRD) pattern and (b) Raman spectrum of the	

List of Figures

as-prepared sample shown in Fig. 2.2 (a).....	56
Figure 3.4 (a) TEM image of the α -Fe ₂ O ₃ nanoflakes, (b) HRTEM image of the nanoflakes and (c) The electron diffraction pattern (circled region) of nanoflakes showing the good agreement with the diffraction pattern of α -Fe ₂ O ₃ from the zone axis of $[\bar{4}41]$	57
Figure 3.5 A schematic diagram of the formation and growth of α -Fe ₂ O ₃ nanoflakes.	59
Figure 3.6 Typical field-emission current density–voltage (J – V) curves of the α -Fe ₂ O ₃ nanoflakes films synthesized at 260 °C for 10 hours. Inset shows the F – N plots ($\ln(J/E^2)$ versus $1/E$) accordingly, which exhibits a good linear dependence (solid line is the fitting result).....	61
Figure 3.7 (a) XRD patterns and (b) Raman spectra of the as-prepared sample and Ar plasma treated samples.....	62
Figure 3.8 (a) TEM image of the α -Fe ₂ O ₃ nanoflake before plasma treated, (b) HRTEM image of (a), (c) TEM image of the α -Fe ₂ O ₃ nanoflake after plasma treatment. Inset of (c) shows the high resolution TEM image the highlighted part.....	64
Figure 3.9 (a) Dark-field and (b) Bright-field TEM images of the tip of the α -Fe ₂ O ₃ nanoflake after plasma treatment.....	65
Figure 3.10 (a) Typical FE J – E curves of the α -Fe ₂ O ₃ nanoflakes films before and after 100 W Ar plasma treatments. Inset shows the F – N plots ($\ln(J/E^2)$ versus $1/E$) accordingly, which exhibits a good linear dependence (solid line is the fitting result). (b) Long-term stability measurement of FE property of nanoflake films after Ar plasma treatment.....	67
Figure 4.1 SEM images of the as-prepared sample with heating temperature of (a) 450 °C (b) 500 °C (c) 600 °C and duration of 10 hours. The inset shows high magnification SEM image of the K _{0.33} W _{0.944} O ₃ nanostructures.....	70
Figure 4.2 XRD pattern of the as-prepared sample: nanowire (black) and nanosheet (red).....	71

List of Figures

Figure 4.3 (a) Low magnification TEM image of the $K_{0.33}W_{0.944}O_3$ nanowire. (b) HRTEM image of the nanowires with growth direction [001]. (c) The selected area electron diffraction (SAED) pattern (circled region) of nanowires which indicates good agreement with the diffraction pattern of $K_{0.33}W_{0.944}O_3$ from the zone axis of $[0\bar{2}0]$	72
Figure 4.4 (a) Low magnification TEM image of the PTB nanosheet. (b) HRTEM image of the PTB nanosheet. The inset is the Fast Fourier Transform (FFT) image of lattice fringes in (b).....	72
Figure 4.5 (a) Energy Dispersive Spectrometer (EDS) data for the hexagonal $K_{0.33}W_{0.944}O_3$ nanowire. (b) EDS data for the hexagonal $K_{0.33}W_{0.944}O_3$ nanosheet.....	73
Figure 4.6 Single-crystal Raman spectra of nanowire (black) and nanosheet (red).....	74
Figure 4.7 (a) SEM image of the as-prepared sample with heating temperature of 450 °C and duration of 1 hour. (b) SEM image of the same nanowires in (a) after being heated for an additional 1 hour at 450 °C.....	76
Figure 4.8 (a) SEM image of the as-prepared sample with heating temperature of 550 °C and duration of 1 hour. (b) SEM image of the same nanowires in (a) after being heated for an additional 1 hour at 550 °C.....	77
Figure 4.9 (a) I_{ds} - V_g curves of the single PTB nanowire transistor as a function of gate voltage V_g at source-drain voltage $V_{ds} = 3$ V. (b) Plots of source-drain current I_{ds} vs. voltage V_{ds} at different gate voltage V_g	79
Figure 4.10 (a) Schematic diagram of setup for the polarized Raman scattering characterization, (b) Optical image of individual $K_{0.33}W_{0.944}O_3$ nanowire, (c) Polarized Raman spectra of the nanowire shown in (b), (All peaks were normalized to the strongest peak locating at 790 cm^{-1}) (d) and (e) Raman mapping images of the nanowire shown in (b) by plotting the intensity ratio between the W = O stretching bands to the O – W – O stretching bands with different polarization geometries as illustrated.....	82
Figure 4.11 Typical FE J - V curves of $K_{0.33}W_{0.944}O_3$ nanowire films. Inset shows the F - N plots ($\ln(J/E^2)$ versus $1/E$) accordingly, which exhibits a good linear dependence; (b) Long-term stability measurement of FE property of nanowire film samples shown in Fig.	

List of Figures

3.6 (a).....	84
Figure 5.1 SEM images of the individual PTB nanowires attached to the electrochemically etched W tip.....	87
Figure 5.2 SEM images of FE measurements as different anode types. (a) Flat plane anode: the diameter of nanowire is 104 nm and length is around 7.2 μm . (b) Needle tip anode: the diameter of nanowire is 86 nm and length is around 7.6 μm	88
Figure 5.3 The I - V curves of individual PTB nanowire with flat plane anode setup (a) and needle tip anode setup (b). (c) and (d) The F - N plots ($\ln(I/V^2)$ versus $1/V$) accordingly, which also exhibits a good linear dependence.....	91
Figure 5.4 The relationship between β and the inter-electrode distance d with flat plane anode setup (black) and the tip anode setup (red), shows increasing enhancement with increasing distance. (a) The calculated results. (b) The finite element simulated results.....	92
Figure 5.5 The SEM images of FE measurements as different angles between the nanowire cathode and the needle tip anode.....	93
Figure 5.6 (a) The relationship of experimental and finite element simulated results between field enhancement factor (β) and the angle α . (b) The finite element simulation of the electric field distribution accordingly.....	94
Figure 5.7 The simulation configuration of off-axis angle γ vs. enhancement factor β	95
Figure 5.8 (a) The relationship of finite element simulated results between β and the angle γ . (b) The finite element simulation of the electric field distribution accordingly.	95
Figure 5.9 Emission properties of the triode type FE setup. (a) Relation of the current I_{esd} vs. applied voltage (V_{esd}) at various V_{eg} as indicated and (b) F - N plot for various V_{eg} as indicated. (c) Plots of FE current I_{esd} and the gate leakage current I_{eg} as a function of side-gate voltage V_{eg} at applied voltage $V_{\text{esd}} = 400$ V in the FE experiment. (d) Curve of the transconductance g_m of the FE setup as a function of side-gate voltage V_{eg}	95
Figure 5.10 Simulated electric field distribution plot in the PTB nanowire emitter cap under constant anode voltage 400 V. (a) The double-side gate-controlled individual	

List of Figures

PTB nanowire FE. (b) The single-side gate-controlled individual PTB nanowire FE.
The white and blue colors represent the lower potential area.....99

Figure 5.11 Calculated results of β for the double-side-gate setup (■) and the
single-side-gate setup (●) with different gate voltage.....100

List of Tables

LIST OF TABLES

Table 1.1 Important field-emission performance parameters and work function of several metal oxide semiconductor nanostructures reported in the literature.....37

Table 1.2 Important evaluating indicators of FE properties for individual metal oxide nano-emitters..... 38

Table 5.1 Relationship between gate voltage (V_{eg}), turn-on voltage (V_{to}) and effective-field-enhancement factor (β) of the gate-controlled individual PTB nanowire FE devices..... 96

List of symbols

LIST OF SYMBOLS

E_F	Fermi energy
E_g	Band gap energy
λ	Wavelength
ϕ	Work function
β	Field enhancement factor
g_m	Transconductance
k	Boltzmann's constant

CHAPTER I INTRODUCTION

1.1 Background

Study on nanomaterials or nanostructures which are defined as objects with at least one dimension on the scale of 0.1 to several hundred nanometers (10^{-9} meter), is one of the most attractive research topics in recent years. Nanomaterials including organic and inorganic based materials, such as copolymer, carbon based materials and metal oxides, are on the nanoscale of morphological features and believed to be essential for much of modern science and technology.¹ The technique to control these nanoscale materials in chemical or physical processes on molecular and molecular cluster scale is called nanotechnology. It covers a very diverse range, from novel extensions of conventional device physics, to new approaches based upon molecular self-assembly, to advanced development of new materials, even to speculation on toxicity and environmental impact of human society. The famous physicist, Noble laureate Richard Feynman described two fundamental approaches to define nanotechnology in a talk named "There's Plenty of Room at the Bottom" on December 29, 1959, called "top-down" which is based on stacking, patterning by lithography, and etching techniques, and "bottom-up" which is on the basis of chemical synthesis and subsequent assembly. In this talk, he considered a process by which the ability to manipulate individual atoms and molecules to form nanomaterial or nanostructure might be developed, using one set of precise tools to build and operate another proportionally smaller set, so on down to the needed scale. This talk was looked as the source of inspiration for the concept of "Nanotechnology".

Although fruitful efforts have been made in these fields, both challenges and development potential still exist. The problems, how to fabricate suitable nanomaterials with convenient, low cost and mass productive method, how to

CHAPTER I Introduction

understand the relationships between the special physical or chemical properties of materials and their morphology or chemical compositions, and how to fabricate relative multifunctional nanodevices based on these materials for future applications, have not been resolved yet. This dissertation shows some useful explorations on the controllable synthesis of nanomaterials, and the relative physical properties of the as-obtained nanostructures.

1.2 Metal oxide nanostructures

Metal oxide materials, especially transition metal oxide, due to their unique electronic properties, are widely used in central processing unit (CPU), static random-access memory (RAM), and other electronic applications.² The transition metal elements are able to form a large diversity of oxide compounds, such as WO_3 , Fe_2O_3 and MnO_3 , which would exhibit metallic, semiconducting, or insulating properties.³ Some special metal oxides exhibit a metal-insulator transition, obtained by varying temperature or pressure.⁴ A number of transition metal oxides can demonstrate superconductivity below certain temperatures.⁵ A vast number of geometrical structures can be represented by metal oxide materials, especially structures at nanoscale. Compared to traditional bulk metal oxide materials, these nanomaterials or nanostructures show special chemical and physical properties, such as self-assembly, self-cleaning, super-hydrophilic, super-hydrophobic properties *etc.* These metal oxide nanostructures with high aspect ratio (i.e., size confinement in two directions) offer better crystallinity, higher integration density, and lower power consumption in device physics.⁶ Due to the large surface-area-to-volume ratios and the small sizes comparable to Debye length,⁷ they demonstrate superior sensitivity to surface chemical processes. In addition, their size confinement renders tunable band gap, higher optical gain and faster operation speed.⁸ These nanostructures can be categorized to different types due to different standards of classification. According to dimensionality, they can be categorized as zero dimension (0D), one dimension (1D)

CHAPTER I Introduction

and two dimension (2D) structures; according to formation method, they can be categorized as vapor-phased synthetical nanostructures, liquid-phase synthetical nanostructures and solid state synthetical nanostructures; according to morphologies, they can be categorized as nanoparticles, nanorods, nanowires, nanobelts or nanoribbons, nanotubes, nanocables, nanocones, nanoflowers and so on. Here in this dissertation, we will discuss metal oxide nanostructures according to different dimensionality as follows.

1.2.1 Classification of metal oxide nanostructures

Depending on the relative sizes of the materials in different spatial directions, metal oxide nanomaterials can be classified as zero-dimension, one-dimension and two-dimension structures. Zero-dimensional (0-D) nanostructures are the objects such as the quantum dots^{9, 10} and nanoparticle whose scale is confined to nanometer regime in all spatial dimensions. According to their structures, they would have transitional properties that are between those of bulk materials and those of discrete molecules. One-dimensional (1-D) and quasi-one-dimensional (Q1D) nanostructures such as the nanowire (NW), nanorod, nanoneedles, nanobelts,¹¹ and nanotube (NT) exhibit promising properties and potential applications in magneto-electronic devices,¹² room temperature UV-lasing devices¹³ and high-density information storage devices.¹⁴ Two-dimensional (2-D) nanostructures such as nanoflake,¹⁵ nanowalls¹⁶ and nanodisk¹⁷ have been extensively studied by the semiconductor community because of their convenient production and usability for commercial fabrication.¹⁸

In particular, it is generally accepted that 1D and Q1D metal oxide nanostructures provide a good system to investigate the dependence of electrical, thermal and mechanical properties on dimensionality and size reduction. As such, 1D and Q1D metal oxide nanostructures, referring the metal elements composition, will show different physical and chemical properties leading to their unique applications.¹⁹ In what follows, we will briefly introduce some examples of 1D and Q1D metal oxide

CHAPTER I Introduction

nanostructures including iron oxide, tungsten oxide and alkali metal doped tungsten oxide nanostructures as the focus point of this thesis.

1.2.2 One-dimensional metal oxide nanostructures

In the family of 1D and Q1D nanostructured metal oxides, iron oxide with great significance in many fields of application is one group of widely studied candidates.¹ Also, tungsten oxide and alkali metal doped tungsten oxide materials have been the subject of numerous studies.²⁰⁻²⁵ The basic material properties and applications of these two kinds' nanostructures are briefly introduced as follows.

1.2.2.1 Iron oxide

Iron oxide is one of the most industrially important materials and shows numerous potential applications, such as the active component of gas sensors,²⁶ photocatalyst²⁷ and enzyme immunoassay.^{28, 29} It has three mineral forms: wüstite (FeO), magnetite (Fe₃O₄) and ferric oxide (Fe₂O₃). The ferric oxide includes four types: α (hematite), β , γ , and ϵ (maghemite). Their physical and chemical properties are totally different: FeO is almost nonstoichiometric with some Fe atom deficiency and can be denoted as Fe_{1-x}O. Fe_{1-x}O has unusual electronic properties as one kind of semiconductors whose carrier type changes from *p* to *n* type around $x = 0.08$.³⁰ Among these iron oxide materials, α -Fe₂O₃ (hematite), a *n*-type semiconductor ($E_g = 2.1$ eV) is the most stable phase under ambient condition.³¹ Hematite crystallizes in the rhombohedral system (space group = R3c) and usually in a hexagonal structure.³² In this structure, alternating iron bilayers and oxygen layers are all parallel to the (001) basal plane (oxygen, white; iron, red and hexagonal unit cell, blue in Fig. 1.1).

CHAPTER I Introduction

Figure 1.1 Crystal structure model of $\alpha\text{-Fe}_2\text{O}_3$ viewed in $[110]$ direction.³³

As $\alpha\text{-Fe}_2\text{O}_3$ bulk materials are non-toxic and corrosion-resistant, they are widely used in many fields. For instance, $\alpha\text{-Fe}_2\text{O}_3$ can serve as a photo-anode in the photo-assisted water electrolysis process due to its abundance, stability, and environmental compatibility, as well as suitable band gap and valence band edge position.³⁴ On this account, Vayssieres *et al.*^{35, 36} used a solution method to synthesize hematite nanorod and it is found that these 1D $\alpha\text{-Fe}_2\text{O}_3$ nanostructures enhanced photoconversion efficiency and improved photovoltaic response speed. The other 1D and Q1D nanostructures of $\alpha\text{-Fe}_2\text{O}_3$ ^{15, 31, 37-41} are fabricated through a variety of methods, such as templating,^{42, 43} hydrothermal synthesis,⁴² thermal decomposition,⁴³ and sol-gel techniques.⁴⁴⁻⁴⁶ The efforts in previous works have been made to lower the growth temperatures of 1D $\alpha\text{-Fe}_2\text{O}_3$ nanostructures from 800 to 400 °C^{31, 40} and simplify the experimental process, but some of growth processes are still rather complicated. Fu *et al.*³⁷ synthesized hematite nanowire arrays by heating iron foil in a special oxidization atmosphere: a gas mixture of CO_2 (19.30%, in volume), SO_2 (0.14%), NO_2 (80.56%) and H_2O vapor. In these processes to synthesize nanowires,

CHAPTER I Introduction

the pressure and flow rate of the gas mixture need to be precisely controlled. In order to explore novel ways to synthesize 1D or Q1D α -Fe₂O₃ nanostructure, Zhu *et al.*¹⁵ reported the fabrication of aligned flake-shaped hematite nanostructures on the surface of atomic force microscope (AFM) tip made from silicon. A typical scanning electron microscope (SEM) image of an as-grown sample is shown in Fig. 1.2, the whole surface of the AFM tip uniformly covered by one layer of flake-like nanostructures. The nanoflakes are aligned almost perpendicularly to the local substrate and have an average length of about 1 μ m. The inset of Fig. 1.2 shows a high magnification SEM image of the tip portion, in which it can be seen that the nanoflakes have very a sharp tip with average diameters of 17 ± 5 nm. At the root of nanoflakes, the width reaches about 100 nm. The thickness of nanoflakes varies within 10–20 nm from tip to root. They are confirmed to be α -Fe₂O₃ by X-ray diffraction (XRD), transmission electron microscope (TEM) and other crystal characterization methods. Its field emission properties will be introduced in Section 1.3.5. These results indicate that heating metal on a hotplate is an effective way to fabricate homogeneous α -Fe₂O₃ nanostructures at low temperature. This may serve as the basis for further improvements. Therefore, to explore a novel fabrication method with mass production, rapid growth, catalyst-free and reasonably low cost to synthesize α -Fe₂O₃ nanostructures is one of the research focuses in my Ph. D study.

CHAPTER I Introduction

Figure 1.2 Typical SEM image of α -Fe₂O₃ nanoflakes on an AFM tip. Inset shows a high magnification SEM image of the tip apex.¹⁵

1.2.2.2 Tungsten oxide and alkali metal doped tungsten oxide

Tungsten oxide (WO₃), also known as tungsten trioxide or tungstic anhydride, is a chemical compound containing oxygen and the transition metal tungsten. WO₃ exists in a large variety of crystal structures, a typical one consists of WO₆ octahedra arranged in various corner-sharing or edge-sharing configurations (Fig. 1.3).^{47, 48} The monoclinic phase instead of a cubic structure appears to be the most stable WO₃ phase among all these crystal structures at room temperature.⁴⁹ WO₃ is also a *n*-type semiconductor with the work function of 5.7 eV⁵⁰ and the direct band gaps lie at 3.52 and 3.74 eV, with an indirect band gap at 2.62 eV.⁵¹ Therefore, the WO₃ material has been applied in many promising applications as an electrochromic device,⁵² semiconductor gas sensor⁵³ and photocatalyst.⁵⁴

CHAPTER I Introduction

Figure 1.3 The structural motif of the arrangement of WO_6 octahedral in the (a) cubic (b) orthorhombic and (c) hexagonal phases of tungsten trioxide.⁴⁸

Recently, 1D and Q1D WO_3 , such as nanowires, nanoribbons and nanoneedles have been successfully synthesized.²²⁻²⁴ Liu *et al.*²³ reported the process of heating a tiny tungsten wire partly wrapped with melted boron oxide (B_2O_3) vitreous powder at 1600 °C in nitrogen atmosphere to produce tungsten oxide nanowire. The B_2O_3 does not serve as a catalyst in this reaction process but as a source of oxygen. It is because its melting point is around 600 °C and boiling point is 1100 °C, which is much lower than the reaction temperature. The formation of tungsten oxide nanowire regardless of catalyst is attributed to vapor-solid growth mechanism, which will be introduced in Section 1.2.3. Li and his co-workers⁵⁵ developed a infrared irradiation heating method to prepare the quasi-aligned single-crystalline $\text{W}_{18}\text{O}_{49}$ nanotubes or nanowires under different vacuum conditions. The diameters of the nanotubes are in the range of 150-350 nm, while those of the nanowires are about 20-100 nm. Also, Hong *et al.*²² reported that the synthesis of high quality tungsten oxide nanoribbons by oxidizing a tungsten plate under moist conditions at 650 °C. Although potassium (K) or other alkali ionic salts are believed to be catalysts²² for producing WO_3 nanostructures in plenty of tungsten oxide nanostructure synthesis works, a lot of problems still have not been solved yet. What is the real role of alkali salts in the fabrication process? Are these chemicals doping into the WO_3 nanostructures? Therefore, we will try to design a simple synthesis method to settle these problems. The experimental details will be introduced in Section 2.1.

CHAPTER I Introduction

Due to their Drude-type optical behavior,⁵⁶ semiconducting to metallic transition,⁵⁷ photochromic,⁵⁸ and superconducting properties at sub-liquid helium temperature,⁵⁹⁻⁶¹ alkali metal doped tungsten oxide materials (also called alkali tungsten bronzes) have received much attention in recent years.^{62,63} In particular, the hexagonal alkali tungsten bronzes $A_x\text{WO}_3$ (HTBs, $A = \text{Li, Na, K, Rb, Cs}$) have a three-dimensional WO_3 lattice made up of corner-sharing WO_6 octahedra, and the alkali cations A^+ are located in the hexagonal tunnels of the lattice (Fig. 1.4). The maximum x value is around $1/3$ in $A_x\text{WO}_3$ when all the alkali atom sites in the hexagonal tunnels are occupied. For instance, when K^+ ions are added to WO_3 , they donate their $4s$ electron to the $\text{W } 5d$ band, rendering bulk metallic behavior at the Fermi level for $x \geq 0.3$.^{51,64,65} For $x < 0.3$, the potassium tungsten bronzes (K_xWO_3), formed by introducing K^+ ions in WO_3 , are n -type semiconductors.⁵⁸ Next I would like to introduce the fabrication methods of these tungsten bronze materials.

Figure 1.4 The diagram of cross-section view in the ab plane perpendicular to the c axis when the potassium ions (blue ball) occupy these hexagonal WO_6 octahedral (yellow tetragon) channels. The structure is filled at $x = 0.33$.⁶⁶

The traditional methods for preparing bulk tungsten bronze materials require rather complicated and harsh reaction conditions.^{25, 58, 62, 67-69} Vakarin group²⁵ studied the

CHAPTER I Introduction

growth anisotropy and the morphology of the single crystals potassium-lithium oxide tungsten bronze fabricated at 700 °C. Also, Reich *et al.*⁵⁸ reported that they can obtain single-crystal WO₃ doped with Na⁺ ions at their surface. This kind of crystals exhibits a sharp decrease in the resistivity when the temperature is lowered to 90 K and a sharp diamagnetic step in the magnetization at around 91 K. This result indicates a possible superconducting property of the crystals. Although the syntheses of tungsten bronze materials are focused on bulk material and amorphous films, there is on-going interest on the synthesis of the 1D and Q1D A_xWO₃ crystalline nanostructures.^{20, 21, 66, 70} For instance, Gu *et al.*²¹ demonstrated a novel hydrothermal synthesis method to fabricate large amounts of single-crystal K_xWO₃ tungsten bronze nanowires. It is found that the morphology and crystallographic forms of the final products are strongly dependent on the sulfate and citric acid, which may act as structure-directing and soft-reducing agent, respectively. Qi *et al.*⁷⁰ provided an alternative technique for the synthesis of highly oriented potassium doped tungsten oxide nanowires by heating tungsten metal with potassium iodide, or bromide, in air at 650 °C. They believe that the nanowire formation process follows the Vapor-Liquid-Solid mechanism, which is going to be introduced in Section 1.2.3. However, the fabrication procedures of A_xWO₃ nanostructures are quite complicated and the expense is very high in most part of previous works. We will discuss a novel one step and low cost fabrication method later in Chapter III.

In this section, literature review on 1D and Q1D metal oxide nanostructures, especially iron oxide and tungsten bronze, are summarized. As research on these nanostructures is indisputably significant, it is worth to investigate the growth techniques and mechanisms in order to fabricate them effectively.

1.2.3 Growth of one-dimensional metal oxide nanostructures

1D and Q1D transition metal oxide nanostructures are obtained through many kinds of physical and chemical methods including vapor phase growth and solution-phase

CHAPTER I Introduction

growth. The high temperature vapor phase growth methods are most widely developed, such as thermal chemical vapor deposition (CVD),⁷³ direct thermal evaporation,⁷¹ pulse-laser-deposition (PLD),⁷² and metal–organic chemical vapor deposition (MOCVD),⁷³ etc. Fig. 1.5 shows the thermal CVD setup consisting of a horizontal quartz tube in a multi-temperatural zones furnace. Source material is placed in reaction boat at high temperature region inside the tube; substrates (Si, SiO₂, etc.) deposited with/without catalyst are located at lower temperature region of the gas flow downstream. However, these traditional CVD methods require not only precise control of the growth parameters, such as atmosphere, flow rate, pressure and substrate position, but also high growth temperature (≥ 1000 °C). It is necessary to further develop low temperature growth methods of metal oxide nanostructures, such as Heat-Oxide method.^{16, 18, 74} In this thesis, we mainly concentrate our research on the extensive use of this Heat-Oxide growth method on different metal oxide nanostructures and the field emission studies of these nanostructures. The developing history of this growth method and two vapor-phased growth mechanisms which could be used to explain the anisotropic growth processes of nanostructures are elaborated in the following section.

Figure 1.5 A schematic diagram of experimental apparatus that is used in vapor phase growth methods including CVD, thermal evaporation, and PLD.⁸

CHAPTER I Introduction

Heat-Oxide method: Heat-Oxide method is a simple spontaneous fabrication method of metal oxide nanostructures by directly heating pure metal source under ambient condition on a hotplate. The growth mechanisms of different nanostructures responsible for this method could be Vapor-Liquid-Solid (VLS), Vapor-Solid (VS), surface diffusion and so on, which will be introduced later. As mentioned before, the traditional CVD method requires complex and precise control of the growth parameters, and thus there is on-going interest to find innovative ways for fabricating metal-oxide-based nanostructures at reasonably low cost in large amounts with good crystallinity and in a simple manner as such. Being at low temperature and catalyst-free method, the Heat-Oxide technique is particularly attractive. Successful attempts have been achieved by this method for a wide variety of nanomaterials, such as γ -ferric oxide,⁷⁵ copper oxide,⁷⁶ hematite,^{15, 18, 77} cobalt oxide,⁷⁴ zinc oxide, molybdenum oxide⁷⁸ and potassium doped tungsten oxide.⁸² I would like to summarize this synthesis method next.

Yu *et al.*⁷⁹ reported that vertically aligned CuO nanowire arrays were successfully fabricated by employing the Heat-Oxide method for the first time. The copper foils are put on the thermal hotplate under ambient atmosphere conditions. The growth temperature is fixed at 400 °C and the duration is 24 hours. These self-assembled CuO nanowires obtained from this new synthesis method have diameters ranging from 20 to 150 nm and lengths of several micrometers. The mechanism that governs in the growth is proposed to be the Vapor-Solid (VS) mechanism as the inexistence of the catalyst. By further polarized micro-Raman scattering characterization on isolated nanowires, the polarization dependence of Raman modes is dominated by the adjustment of the electric inside nanowires. Followed the same growth method, Zhu and his co-workers⁷⁶ explored the field emission (FE) properties of these CuO nanowire arrays. It is found that these nanowire films exhibit a low turn on field of 3.5–4.5 V/ μm and a large current density of 0.45 mA/cm² under an applied field of about 7 V/ μm .

For extensive use of this Heat-Oxide growth method, Yu *et al.*¹⁸ also reported the application of this method on other metal oxide nanostructures. For instance,

CHAPTER I Introduction

vertically oriented α -Fe₂O₃ nanoflakes can be synthesized by heating a piece of pure iron foil on a hotplate. Optical pictures of the foil during the heating process are shown in Fig. 1.6. Fig. 1.6 (a–c) show the color of the iron foil before heating, after heating at 300 °C for 10 min, and after heating at 300°C for 24 h, respectively. Fig. 1.6 (d–f) show the corresponding SEM images of the surface of the iron foil at different stages of heating. It is clearly seen that the surface of the iron foil covered by a layer of flake-shaped nanostructures after suitable long heating duration. Chemical composition of these nanoflakes is confirmed to be α -Fe₂O₃ by XRD, Raman spectroscopy and TEM. The α -Fe₂O₃ nanoflakes fabricated by similar method grown on sharp W tips¹⁸ and AFM tips¹⁵ exhibit promising electron FE properties. Although the large scale α -Fe₂O₃ nanoflake film sample has been successfully fabricated by this Heat-Oxide method, until today, there is no report on effective FE from this kind of film samples which may have more promising potential applications yet. In the current thesis, we attempt to solve this problem by a low temperature growth method. The attempts on fabrication of PTB nanostructures are also made by using a similar method. The details will be described in Chapter III and IV.

Until now, CuO nanowires, ZnO nanoflowers, Co₃O₄ nanowalls, Fe₂O₃ nanoflakes, MoO₃ nanowires and potassium doped WO₃ nanowires have been successfully synthesized by employing the Heat-Oxide method. It is noticed that this method has benefits such as substrate-friendly, low-formation temperature, diversity of materials made, ease of nanomaterials assembly onto various substrates for further characterization and applications.¹⁸

CHAPTER I Introduction

Figure 1.6 (a-c) Optical images of the pure iron foil (10 cm × 10 cm) a) before heating, b, c) after heating at 300 °C for 10 min and 24 h, respectively. (d-f) Corresponding SEM images of foil surfaces shown in (a-c). The size of the α -Fe₂O₃ nanoflake gradually increases with the heating duration.¹⁸

Next we will introduce two classical anisotropic growth mechanisms: Vapor–Liquid–Solid (VLS) and Vapor–Solid (VS) mechanism. These two mechanisms are widely used to explain most parts of vapor-phase growth of 1D and Q1D nanostructures.

1) Vapor-Liquid-Solid (VLS) growth

The VLS mechanism was first proposed by Wagner and Ellis in 1964 while observing the growth of Si whisker.^{80, 81} This process is one kind of catalyst-assisted growth which uses alloy nucleation as seeds. These seeds whose sizes are determined by the temperature and the interfacial energy, crystal growth direction and diameter of nanostructures could be easily controlled by the deposition parameters. In the case of

CHAPTER I Introduction

growing 1D and Q1D metal oxide nanostructures, both the catalyst and source metal firstly form a liquid alloy droplet at high temperature. Precipitation occurs when the liquid droplet becomes supersaturated with source metal. Under the concomitant oxygen gas flow, metal oxide nuclei are formed.⁸² The growth begins after the formation of the nuclei and continues along one particular crystallographic orientation as long as appropriate quantities of oxygen gas and source metal reactants are available, which leads to the 1D nanostructure (Fig. 1.7). This VLS 1D growth process have been observed directly in the *in situ* TEM⁸³ by P. D. Yang's group⁸⁴ and many other researchers.

Figure 1.7 The proposed 1D metal oxide nanostructure growth model. (A) The liquid metal alloy droplet formation and the O_2 in the inlet flow absorbed and reacted to the alloy. (B) Liquid metal oxide supersaturated and precipitated nanoclusters which serve as nuclei. (C) The growth of 1D metal oxide nanostructure continues along one particular crystallographic orientation. (D) Growth terminates when the source metal is exhausted.⁸³

2) Vapor-Solid (VS) growth

VS growth process of nanostructures from gas phase reactants could be possible even in the absence of any metal catalyst which is usually considered as self-catalyzed growth. This growth process has been observed by many research groups.^{85, 86} The VS mechanism could be used to explain the growth of 1D or Q1D nanostructures which

CHAPTER I Introduction

are proposed to minimize the surface free energy of one particular crystal direction.⁸⁷
⁸⁸ When the furnace temperature goes high enough, the source materials would be vaporized directly, then brought by the carrier gas to react with oxygen and condense on the substrate which is located in the low temperature region. The initially condensed molecules act as a self-catalyst, form the nuclei of nanostructures on substrates, and finally facilitate directional growth in order to minimizing the surface energy.

The solution-phase growth of 1D and Q1D metal nanostructures have also been successfully demonstrated. Template-assisted synthesis with anodic aluminum oxide (AAO) membranes,⁸⁹⁻⁹² electrochemical deposition,⁹³ sol-gel deposition,⁹⁴ surfactant-assisted growth,⁹⁵ and hydrothermal growth⁹⁶ have been widely used to produce 1D and Q1D metal oxide nanostructures. Here, we do not discuss the details of these growth methods because of the limited space in this thesis.

1.2.4 Modification of one-dimensional metal oxide nanostructures

In order to enhance the performance of 1D and Q1D metal oxide nanostructures in acoustical, optical, magnetical and electrical applications, suitable chemical and physical modification is indispensable. These modification methods are not only conducted during synthesis process but also in post-synthesis process. Element doping and reactive ion etching (RIE) are two conventional methods to modify the intrinsic and extrinsic properties of these nanostructures.

1.2.4.1 Doping of 1D metal oxide nanostructures

It is effective to influence the electrical properties of 1D and Q1D nanostructures through doping procedures. To produce high quality *n*- and *p*-type metal oxide nanomaterials, it is pivotal to control doping elements and doping profile. Fan *et al.*⁹⁷ reported successfully controlled *p*- and further enhanced *n*-type doping of natural

CHAPTER I Introduction

n-type α -Fe₂O₃ nanobelts. The element Zn is chosen as the dopant. It is found that the α -Fe₂O₃ nanobelt can be easily doped with Zn and converted to *p*-type semiconductor at 700 °C. Fig. 1.8 (a) plots the *I*-*V* and *I*-*V_g* curves of α -Fe₂O₃ nanobelt after doping. The phenomenon that the increase of gate voltage results in the decrease of source-drain current indicates the classical *p*-type property in the nanobelt (inset of Fig. 1.8 (a)). It is also observed that the *n*-type α -Fe₂O₃ nanobelt with enhanced carrier concentration and mobility could be obtained by doping Zn at 350 °C as shown in Fig. 1.8 (b). Its electrical conductivity is enhanced four orders of magnitude higher than that of the nanobelts before doping. The *p*-type doping effect is attributed to the substitution of Fe³⁺ by Zn²⁺ ions in α -Fe₂O₃ crystal structure at high temperature which consequently increases the hole concentration in it. Comparatively, at low temperature, the elemental Zn introduced onto the surface of the nanobelts serves as an electron donor thus contributing to enhance *n*-type conductivity. For both of these *p*-type and *n*-type doping, the doping effect on the hole and electron transport, yielding the Schottky barrier between the contact of metal electrode and materials, give rise to the non-linear *I*-*V* curves.

Figure 1.8 (a) *I*-*V* curves of the *p*-type α -Fe₂O₃ nanobelt devices doped with Zn source at 700 °C (inset is *I*-*V_g* curve). (b) *I*-*V* curves of the enhanced *n*-type α -Fe₂O₃ nanobelt devices doped with Zn source at 350 °C (inset is *I*-*V_g* curve).⁹⁷

CHAPTER I Introduction

1.2.4.2 Reactive ion etching (RIE) treatment on 1D metal oxide nanostructures

RIE treatment is one kind of plasma etching technique. It could be employed to change the surface morphology and chemical composition of materials. The mechanism of this treatment will be described in Section 2.3. Recently, experiments have shown that emission current density of carbon nanotubes (CNT) could be effectively enhanced by RIE treatments, which are capable of functionalizing and modifying the surface structure of CNT.⁹⁸ In addition, plasma in H_2 ,⁹⁹ Ar,¹⁰⁰ O_2 and CF_4 ¹⁰¹ atmosphere have also been adopted to modify nanomaterials.

Zhu and his co-workers¹⁰¹ investigated the effects of tetrafluoro methane (CF_4) and oxygen (O_2) plasmas on the CuO nanowires. Fig. 1.9 shows the TEM images of CuO nanowires before and after plasma treatments. More than half of the as-grown nanowires have a flat tip as shown in Fig. 1.9 (a). Almost all the as-grown nanowires are covered by an amorphous layer with the thickness of several nanometers (inset of Fig. 1.9 (a)). The chemical composition of such layer is also CuO. Subsequently, after 10 min of O_2 (Fig. 1.9 (b)) and CF_4 (Fig. 1.9 (c)) plasma etching, almost all nanowire tips are sharpened. Moreover, the amorphous layers on the tip surface region disappeared after the plasma treatment.

Figure 1.9 (a) TEM image of an as-grown CuO nanowire. The inset shows a high resolution TEM image from the tip part. (b) TEM image of a CuO nanowire after exposure to 10 min of O_2 plasma. Insets are the HRTEM images of different parts. (c) TEM image of a CuO nanowire after 10 min of CF_4 plasma.¹⁰¹

CHAPTER I Introduction

Fig. 1.10 (a) shows the FE current density vs. electrical field (J - E) curves of the same CuO nanowire sample before O_2 plasma RIE treatment, after exposure to O_2 plasma for 5 and 10 min. Under the same electric field ($5.3 \text{ V}/\mu\text{m}$), the maximum J increases from the original 0.13 to $0.34 \text{ mA}/\text{cm}^2$ after 5 min etching, and another 5 min RIE further enhances it to $0.54 \text{ mA}/\text{cm}^2$. At the same time, the turn on field E_{to} (defined by the J of $10 \mu\text{A}/\text{cm}^2$) decreases from the original 3.6 to 3.2 and $3.0 \text{ V}/\mu\text{m}$ after 5 and 10 min O_2 plasma treatments, respectively. The maximum FE J is enhanced 25 times from 0.04 to $1 \text{ mA}/\text{cm}^2$ after 10 min of exposure to CF_4 plasma treatment in another CuO nanowire sample. E_{to} is reduced from 4.2 to $3.7 \text{ V}/\mu\text{m}$ (Fig. 1.10 (b)).

Figure 1.10 (a) Typical FE J - E curves and F - N plots (inset) of as-grown and O_2 plasma-treated CuO nanowires. (b) Typical FE J - E curves and F - N plots (inset) of as-grown and CF_4 plasma-treated CuO nanowires.¹⁰¹

Sung and his co-workers⁹⁹ reported similar effects on the FE characteristics of CuO nanowires after hydrogen plasma treatment. E_{to} , corresponding to the J of $0.1 \mu\text{A}/\text{cm}^2$, is decreased with increasing plasma treatment duration as shown in Fig. 1.11. The effect of hydrogen plasma treatment is different from that of O_2 and CF_4 plasma treatments. The hydrogen plasma would reduce CuO to metal Cu to lower the surface

CHAPTER I Introduction

potential barrier and clean the amorphous layer on the surface of CuO nanowires. These processes will further decrease the E_{to} in FE process.

Figure 1.11 Typical FE J - E curves of CuO nanowires with H_2 plasma treatment; untreated, treated for 5, 10 and 15 min.⁹⁹

1.2.5 Applications of one-dimensional metal oxide nanostructures

1D and Q1D metal oxide nanostructures have yielded substantial practical applications: chemical/biochemical sensors,¹⁰² industrial catalyst and field effect transistors,⁹⁷ optoelectronic devices,¹⁰³ piezoelectric devices,^{104, 105} lasing devices,¹³ FE devices,¹⁰⁶ etc. due to their novel chemical and physical properties.¹⁰⁷ We will summarize the applications of these nanostructures in detail.

1.2.5.1 Chemical sensor

The chemical sensing behaviors and catalysis capabilities are well-known properties of metal oxide materials. The electronic property of 1D and Q1D metal oxide nanostructures, with a large surface-area-to-volume ratio and one certain dimension comparable to Debye length, is strongly influenced by the chemical reactivity of

CHAPTER I Introduction

surface sites, yielding more sensitivity than their thin film counterpart.¹⁰⁸ Many research groups contribute to this field. Kim *et al.*¹⁰² reported that drop-coating nonstoichiometric tungsten oxide ($\text{WO}_{2.72}$) nanorod-based films with active adsorption sites show highly sensitive sensing ability for various reducing and oxidizing analytes even at room temperature. When reducing gases exposure, the temperature-dependent response is reversed from decrease in the sensor resistance at higher temperature to increase at lower temperature. The facile vapor detection of $\text{WO}_{2.72}$ nanorod sensors at ambient temperatures might be employed for miniaturized sensing system fulfilling the requirement of low power consumption.

1.2.5.2 Field effect transistors

The electrical transport property is one of the most important physical properties for the 1D and Q1D metal oxide nanostructures because these materials are the best choice for fundamental building blocks of nanoscale electronic devices and circuits.¹⁰⁹ Semiconducting nanowires can be used as active electric elements in the field effect transistor (FET),¹¹⁰⁻¹¹² insulating nanowire can be used as dielectric layer of gating electrodes; metallic nanowires are suitable as electrical interconnects or nanoelectrodes. Fan *et al.*⁹⁷ reported that fabrication and characterization of *n*-type $\alpha\text{-Fe}_2\text{O}_3$ nanobelt FET. Fig. 1.12 (a) shows a schematic of a nanobelt FET with metal contacts functioning as the source and drain electrodes, and Si as the back gate. It is found that similar to ZnO and In_2O_3 , native oxygen vacancy renders $\alpha\text{-Fe}_2\text{O}_3$ nanobelts *n*-type semiconducting behavior, as shown in Fig. 1.12 (b).

CHAPTER I Introduction

Figure 1.12 (a) a schematic diagram of experimental setup testing a nanobelt FET. (b) I - V_{ds} characteristics of α - Fe_2O_3 nanobelt FET obtained at back gate potentials of -10 V, 0 V, and 10 V. Bottom inset: Energy band diagram of Ni- Fe_2O_3 nanobelt contact, ϕ is the work function. Top inset: I - V_g curve of the nanobelt FET obtained at 2.0 V source-drain bias.⁹⁷

Most metal oxide nanomaterials behave like a semiconductor or an insulator,¹¹⁴⁻¹¹⁶ however, few with metallic property is reported. Based on the electronic structure of alkali tungsten bronzes, the PTB nanowire would show metallic property which will be worth investigating systemically. The device fabrication and characteristic details will be described in Chapters II and III, respectively.

1.2.5.3 Optoelectronics

As a wide-gap n -type II-VI group semiconductors ($E_g = 3.37$ eV), ZnO has a large exciton binding energy of 60 meV, which is larger than the thermal energy at room

CHAPTER I Introduction

temperature (26 meV) and would present substantial interest for optoelectronic applications. Yang *et al.*¹³ reported that ZnO nanowire fabricated by thermal CVD process can be employed as natural laser cavities with diameters varying from 20 to 150 nm and lengths up to 10 μm . With a low lasing threshold of 40 kW/cm^2 under optical excitation, surface-emitting lasing action is observed at 385 nanometers, with an emission linewidth less than 0.3 nm. (Fig. 1.13)

Figure 1.13 Emission spectra from ZnO nanowire arrays below (a) and above ((b) and inset) the lasing threshold, respectively. The pump power for these spectra are 20, 100, and 150 kW/cm^2 , respectively. The spectra are offset for easy comparison.¹³

1.2.5.4 Field emission devices

Field emission (FE) is one kind of electron emission from the surface of solid materials. FE studies based on a wide variety of 1D and Q1D metal oxide nanostructures have been actively pursued by researchers worldwide.¹¹³ It is well known that the local electrical field at the tip of an emitter is much higher than the applied electrical field, which is due to field enhancement effect.¹¹⁴ This enhancement has been demonstrated for many systems and benefited in various applications such as

CHAPTER I Introduction

FE displays, microwave sources, X-ray generator and many more.¹¹⁵⁻¹¹⁷ The details on the FE phenomena and mechanisms will be given below.

1.3 Field electron emission

1.3.1 Electron emission mechanisms

Electron emission occurs when an electron overcomes the surface potential barrier on the material surface to escape into vacuum. There are four types of mechanisms which describe the electron emission from the solid material surface. They are (1) thermionic emission, (2) secondary emission, (3) photoelectric emission and (4) field emission.

Figure 1.14 Electron emission classifications based on emission mechanisms.

1.3.1.1 Thermionic emission

Thermionic emission is one kind of heat-induced electron emission in which the electron flow emits from the material by overcoming the surface potential barrier. The driving force of electron flow across the potential barrier is caused by thermal vibration energy. A classical example of thermionic emission is the vacuum electron tube in which the electrons emit from a hot metal cathode into a vacuum. This phenomenon is also called as the Edison effect. The vacuum tube is crucially

CHAPTER I Introduction

important in the operation of electronic devices but has been replaced by the transistor and the integrated circuit (IC) for decades. Thermionic emission becomes significant only for emitter temperatures over 1000 K. In our experiment setup, we try to keep the emitter temperature at room temperature before FE testing. Also, melting point of our nanostructure is much lower than 1000 K.

1.3.1.2 Secondary emission

Electron emission from a metallic surface by bombardment of high speed electrons or other particles is known as secondary emission. When high speed electrons suddenly hit the metal surface, they may give a part or all of their kinetic energy to the free electrons in the metal. If the energy of the striking electrons is sufficient, the free electron will escape from the metal surface and this phenomenon is called secondary emission. In our FE measuring process, there is no other electron source except our 1D and Q1D metal oxide nanostructures. As such, in our experimental setup, secondary electron emission will hardly happen.

1.3.1.3 Photoelectric emission

Photoelectric emission is also called the photoelectric effect. The photoelectric effect is a quantizing electronic phenomenon in which electrons emit from matter after the absorption of energy from electromagnetic radiation such as X-ray or visible light.^{118, 119} To avoid photoelectric emission, we carry out our field emission experiment in dark vacuum chamber.

1.3.1.4 Field induced emission

Field emission (FE) - also called Fowler-Nordheim (*F-N*) tunneling¹²⁰ - is a form of quantum tunneling in which electrons pass through the potential barrier covered by a high electric field. This phenomenon highly depends on both the material structures

CHAPTER I Introduction

and the shape of the particular cathode. A FE electron source offers brightness more than 100 times higher than conventional thermionic electron sources. The current density of FE can reach 10^7 A/cm² with no time delay in the turn on time. In what follows, we will detail the FE process.

1.3.2 Surface potential barrier

Based on the energy band theory, when a large number of atoms (in the order of 10^{20} or more) are brought together to form a solid, the number of atomic orbital becomes exceedingly large, and the difference of their energy becomes very small, so the levels may be considered to form continuous bands of energy rather than the discrete energy levels of the atoms in isolation. However, no matter how many atoms are aggregated, some energy intervals contain no orbital form forbidden bands or band gaps. The upper most energy level, which is almost fully occupied, is called the valence band by analogy with the valence electrons of individual atoms. The lowermost energy level higher than that of the valence band, which is scarcely occupied, is called the conduction band. Because of the narrow band gaps or lattice defects, semiconductors can exhibit certain conductivity under the thermal excitation or electromagnetic effects (applied electrical or magnetic field). The current can flow in semiconductor materials only when electrons are excited to the conduction band.

Based on the energy band theory, every solid material contains electrons. All electrons are bound inside the solid by surface potential barrier. It is defined as liberation of free electron from a surface of a solid caused only by the external energy transferred to the electrons or the decreasing of the surface potential barrier. The additional external energy required by electron emission could come from a few sources, such as heat energy, energy stored in the electron field, light energy or kinetic energy. The classification of electron emission is mentioned in Section 1.3.1.

For example, free-electron distribution in the metal can be described as a 1D potential well with flat bottom based on quantum mechanics theory. (Fig. 1.15) The

CHAPTER I Introduction

bottom energy level of potential well E_c is the stationary electron energy inner metal (conduction band bottom), and the top energy level E_0 is the stationary electron energy out of the metal (vacuum level of the metal). The difference between E_c and E_0 is the surface potential barrier of the materials, which must be overcome by the electron if the electron is to escape from the surface. E_F is the Fermi level.

Figure 1.15 Schematic diagram of one-dimension potential well with flat bottom.

There are two aspects of the surface potential barrier listed as follows:

1) Electrical double layer formed by the “clouds of electron”

The crystal lattice of the metal is not satisfied with the whole periodic boundary condition any more at the vacuum boundary. Considering the thermal motion of electrons inside metal, some of them try to escape from the metal surface to the vacuum. The electron clouds of metal near its surface will distribute asymmetrically, and the center of them will move near to the outer vacuum. The metal atoms will be polarized to the ions of opposite charge by the asymmetrical electric field. A pair of opposite charge atoms is called a dipole. Two parallel charged layers are formed by uncountable dipoles in the distance X_0 (several atoms space) from the metal surface. They are the positive charged layer on the surface and the oppositely negative charged layer outside the surface. This structure is called the electric double layer. If the free

CHAPTER I Introduction

electrons inside the metal with energies below the Fermi level tunnel through the intermediate surface, the electrical double layer will do work on the electrons and form a surface potential barrier to block the electrons escaping.

2) Image force

The image force is one kind of electrostatic force affecting the tunneling of electrons in the neighborhood of the metal surface. It may be thought of as the attraction from the electron's mirror positive image. This force applied on the electron is very complex near the surface of the metal. This image potential was first explicitly considered by Nordheim on 1928.¹²¹ The image force is another force to block the electrons from escaping the surface.

When the distance between the electron and metal surface is smaller than X_0 , the major effect on the electron is double electrical layers mentioned in Section 1.3.2.1; when the distance is larger than the X_0 , the electron can escape to the vacuum level only after overcoming the image force. The free electron is considered to totally escape from the metal when the distance between them under the no-external applied electric field condition.

As mentioned above, the electron must overcome the surface potential barrier to escape from the metal surface. The minimum energy (usually measured in electron volts) to remove an electron from a solid to a point immediately outside the solid surface (or energy needed to move an electron from the Fermi energy level into vacuum) is defined as work function. Here, "immediately" means that the final electron position in vacuum is far from the surface on the atomic scale but still close to the solid on the macroscopic scale. According to the Bohr-Sommerfeld model,¹²² the electrons at the Fermi level have the greatest energy among all electrons at the temperature $T = 0$ K. It can be calculated that the minimum energy needed to remove an electron from the material surface to the vacuum level immediately:

$$\phi_m = U_a - E_{F0} \quad (1.1)$$

CHAPTER I Introduction

where ϕ_m is the work function (eV), U_a is the surface potential barrier, E_{F0} is the Fermi level energy of the metal when $T = 0$ K.

The surface potential barrier besieged all electrons inside the material is consolidated as the results of these two aspects. We will introduce an efficiency method to liberate the electron through this barrier in the next section.

1.3.3 Fowler–Nordheim (*F-N*) tunneling

As mentioned in Section 1.3.1, field electron emission, sometimes called cold electron emission or Fowler-Nordheim (*F-N*) tunneling,¹²³ is unique in comparison with other emission types. The electrons with energy near the Fermi level have a non-negligible tunneling probability and can move through the potential barrier to the vacuum level in this phenomenon. The *F-N* tunneling is generally used in order to quantitatively describe the FE process for metals, which requires the calculation of FE current density as a function of the electric field. However, in practice, the FE process is very complicated and accurate calculation is a formidable task that can be alleviated by the following main assumptions:

1) The metal is assumed to obey the Sommerfeld free electron gas model with Fermi-Dirac distribution function which will be described later on. It would mean that the highest occupied electron energy levels of the metal are filled up by electrons from the bottom to the Fermi level E_F , and empty above at $T = 0$ K. At non-zero temperature, the calculations show that there is a linear relationship between the work function of a metal and its temperature.¹²⁴ Thus, the relationship between the work function and the temperature is determined by the Fermi level of the metal at different temperatures. Based on these theoretical calculations, the Fermi level E_F can only change 0.1% of E_{F0} from 0 K to 2500 K. Thus the approximation is so tenable that the Fermi level and work function of metal will not change a lot while the temperature varies.

CHAPTER I Introduction

2) The fluctuation on the emitter surface is neglected and the interface between emitter surface and vacuum is assumed to be a flat plane, that is, a one dimensional problem is considered. This assumption is accurate because the thickness of the potential barrier in fields of 10^7 - 10^8 V/cm is several orders of magnitude less than the emitter radius in most cases. Thus, the external field can be taken to be uniform along the surface for the finite surface without considering surface distortion effect.

As shown in Fig. 1.16, potential barriers exist on the interface between the solid surface and the vacuum. The basic principle of the FE is electron quantum tunneling, in which the high external electric field sufficiently narrows and lowers the surface potential barrier of the material until the width of the potential barrier approached the wavelength of electron. The procedure is described as below: At zero electric field, this potential barrier is a step function; its height is denoted as the work function ϕ and its width is semi-infinite (Fig 1.16 (a) (red solid line)). The situation changes when an electric field F is applied. As a result of this external field and the image charge effect,¹²¹ the potential barrier varies from a semi-infinite long step function to the shape with finite width shown in Fig.1.16 (b) (red solid line). Its height is reduced and its width is narrowed. With increasing electric field strength, the width of the potential barrier becomes comparable with the wavelength of the electron so that electrons can tunnel through it.

CHAPTER I Introduction

Figure 1.16 Schematic diagrams of the potential barriers on the interface between the electron emitting surface and vacuum at (a) zero and (b) strong external applied field.

Assuming planar metal surface, the emission current density can be written as,

$$J = e \int_0^{+\infty} E_x N(E_x) D(E_x) dE_x \quad (1.2)$$

where E_x is part of the electron energy due to the momentum perpendicular to metal surface. $E_x N(E_x) dE_x$ is the density of electrons with energies in between E_x and $E_x + dE_x$ incident on unit area of the potential barrier surface from the metal. $D(E_x)$ is the tunneling probability of the incident electron with energy component E_x due to momentum perpendicular to the metal surface. The integral is taken from $0 \rightarrow +\infty$ since the electrons are trapped in the metal for $x < 0$.

Based on the assumption that electrons in metal obey the Sommerfeld free electron gas model with Fermi-Dirac distribution function,¹³ and taking into account of the distribution function and the energies of the electrons in the various directions, the

CHAPTER I Introduction

current density can be rewritten as:

$$J = \frac{2e\pi}{m^2} \int_0^{+\infty} dE_x D(E_x) \int_{E_x}^{+\infty} dE_x f(E_x, T) \quad (1.3)$$

Using Wintzel-Kramers-Brillouin (WKB) approximation¹²⁵ to evaluate the tunneling probability $D(E_x)$,

$$D(E_x) = \exp\left(-2\sqrt{\frac{8\pi^2 m}{h^2}} \int_{x_1}^{x_2} dx \sqrt{e \cdot \phi(x) - E_x}\right) \quad (1.4)$$

where $e \cdot \phi(x) - E_x$ is the difference between the energy of the potential barrier at position x , as shown in the Fig. 1.16.

By evaluating the second integral of equation (1.3) and taking note that majority of the electrons tunneling through the potential barrier are near the Fermi level, we could obtain:

$$\int_{E_x}^{+\infty} dE_x f(E_x, T) = \frac{2k_B T m^3}{h^3} \ln\left(e^{\left(\frac{E_x - E_F}{k_B T}\right)} + 1\right) \quad (1.5)$$

where E_x is the energy of the electron, T is the thermodynamic temperature, and k_B is Boltzmann's constant.

Evaluating $D(E_x)$ and inserting the expression into equation (1.3) with further integration with change of variables, the final form of tunneling current density J for electron passing through a general potential is obtained:

CHAPTER I Introduction

$$J = \frac{4e\pi m k_B T}{h^3} \int_0^{+\infty} dE_x D(E_F) \cdot e^{\left(\sqrt{\frac{8m\pi^2}{h^2}} (E_x - E_F) \right) \int_{x_1}^{x_2} \frac{1}{\sqrt{e\phi(x) - E_F}} dx} \cdot \ln(e^{\frac{E_x - E_F}{k_B T}} + 1) \quad (1.6)$$

Since the resultant potential in Fig. 1.16 (b) look triangular, a triangular potential is assumed in the derivation of the $F-N$ theory.

The resultant potential for the triangular potential at a distance x_2 away from the origin (Fig 1.16 (b) (black solid line)) can be expressed as:

$$e \cdot \phi(x_2 - x_1) = e \cdot \phi + E_F - e \cdot E(x_2 - x_1) \quad (1.7)$$

At the point x_2 ,

$$e \cdot \phi - e \cdot E(x_2 - x_1) = 0 \quad (1.8)$$

With this equation (1.8), we can express the Fowler-Nordheim ($F-N$) current density at $T = 0$ K as the $F-N$ equation:

$$J = \frac{AE^2}{\phi} \exp \left[-\frac{B\phi^{\frac{3}{2}}}{E} \right] \quad (1.9)$$

where the unit of J are A/cm^2 , the unit of E are V/cm , the unit of ϕ are eV ,

$$A = \frac{e^2}{8\pi h} = 1.54 \times 10^{-6} \text{ A V}^{-2} \text{ eV} \text{ and } B = -\frac{8\pi}{3h} \sqrt{2em} = 6.83 \times 10^7 \text{ V cm}^{-1} \text{ eV}^{-3/2},^{126}$$

respectively. It is obvious that the FE current density is related to the field strength on the metal surface and the work function of the metal.

Equation (1.9) also can be transformed to the relationship between the emission

CHAPTER I Introduction

current I and the field strength E :

$$I = \frac{aAE^2}{\phi} \exp \left[-\frac{B\phi^{\frac{3}{2}}}{E} \right] \tag{1.10}$$

where a is the emission area.

From equations (1.9) and (1.10), the slope of the graph of $\ln(J/E^2)$ against (I/E) can be obtained as:

$$\frac{d \ln(J / E^2)}{d(I / E)} = -B\phi^{\frac{3}{2}} \tag{1.11}$$

When the work function of the emitter is confirmed, the relationship between $\ln(J/E^2)$ and (I/E) can be fitted to straight lines. This linear relationship is considered as the symbol of F - N emitting model.

In the FE process, the indicator evaluating the FE properties of materials and devices include the turn on field (E_{to}), the emission current density (J), the stability of emission, and the field enhancement factor (β), which are introduced below (Fig. 1.17).

Figure 1.17 Schematic illustration of evaluating indicator in FE process

CHAPTER I Introduction

1) The turn on field E_{to}

The turn on field (E_{to}) is defined as the value of electrical field at which the electron begins to emit from the solid surface in FE process. Generally speaking, the E_{to} for metal oxide nanostructure FE is the field strength value while the emission current density is $10 \mu\text{A}/\text{cm}^2$. This E_{to} is one of important common evaluating indicators, where unit is $\text{V}/\mu\text{m}$. Its value determines the difficulty of electrons emission when the external field applied between two electrodes. The lower E_{to} means that the easier the FE.

2) The current density J

The current density (J) is defined as the proportion of the FE current to the area of emission. It indicates the capability of FE for emitters. Under the same applied electrical field, the larger current density signifies better FE capability and higher emission efficiency.

3) The stability of emission current

The stability and reliability of the emitter in FE performance can be justified by the variation of the emission current with respect to time. The stability and the reliability are determined by the vacuum level, the environmental gas composition, the chemical and physical properties of the material such as chemical stability, thermal stability and electrical transport stability.

4) The field enhancement factor β

The field enhancement factor, β , is an important parameter to justify the FE properties of the material, which is defined by:

CHAPTER I Introduction

$$E_{local} = \beta E_{mean} = \beta \frac{V}{d} \quad (1.12)$$

where E_{local} is the local electric field nearby the emitter tip, E_{mean} is the mean electric field which is defined as the average electric field between two electrodes, d is the average spacing between the electrodes and V is the applied voltage. The larger field enhancement factor means the higher aspect ratio and the better FE performance of the emitter. In analyzing the results of a practical experiment, the field enhancement factor β can be determined from the slopes (S) of $\ln(J/E^2)$ vs. $(1/E)$ plots as:

$$\beta = -6.83 \times 10^3 \frac{\phi^{\frac{3}{2}}}{S} \quad (1.13)$$

1.3.4 Field emission of one-dimensional metal oxide nanostructures

Since Fowler and Nordheim explained the FE phenomenon in 1928 for first time,¹²³ FE properties of many materials have been studied. To date, thousands of research articles have been published in this research field, which reflects its special importance. In the initial stage of research history, the studies are mainly concentrated on FE properties and applications of metal and carbon based materials.

Since the discovery of Carbon Nanotubes (CNTs) in 1991, they have attracted much attention due to their unique properties. In 1995, several groups found that CNTs could also be excellent electron field emitters, with low turn-on fields and high emission current densities.^{127, 128} Compared with conventional emitters, such as Mo and Si tips, CNTs exhibit lots of desired properties for efficient emitters, including very sharp tip, high aspect length to diameter ratio, robust and stiff structure, long term emission stability and so on.¹²⁹ These could lead to a new generation of flat panel display electron sources. Thus, in the last decade, much effort was devoted to the field emission of CNTs and a large amount of experimental and theoretical results have been reported. The short survey of the CNTs based field emitting devices will be

CHAPTER I Introduction

summarized as follows.

Laser ablation, arc discharge and CVD are three of the most commonly used methods to synthesize CNTs. Especially, CVD method can realize the direct growth of CNTs on certain substrates, with the assistance of metal catalysts like Fe, Co and Ni.¹³⁰ By controlling the position of catalysts, the growth position and population density of CNTs can be controlled by lithography process.¹³¹ So far it has been believed that field emission properties of CNTs do not depend on whether they are single-wall CNTs (SWNTs) or multi-wall CNTs (MWNTs). Normally non-linearity of the $F-N$ plots was observed from CNTs, especially in the high electric field region.¹³² Such a deviation from the $F-N$ behavior of CNTs has been ascribed to different origins, including the non-metallic density of states at the tip,¹³³ space charge effects,¹³⁴ the resistance between emitters and substrates,¹³⁵ non-uniform local field near the tip,¹³⁶ different enhancement factors within emitters,¹³⁷ and so on. Typically, the turn-on field (corresponding to $10 \mu\text{A}/\text{cm}^2$) and threshold field (corresponding to $10 \text{ mA}/\text{cm}^2$) are about 1 and 6 $\text{V}/\mu\text{m}$, respectively.^{138, 139} The maximum current density from CNT films varies between $100 \text{ mA}/\text{cm}^2$ to several A/cm^2 due to different experimental setup configurations and different experimental procedures.^{139, 140}

However, the lack of structure-controlled growth strategies for CNTs is still a challenging issue in device integration. Alternatively, FE emitters based on one dimensional metal oxide nanostructures have attracted attention due to the feasibility of precise structural control during the growth process. In contrast to CNTs, these 1D nanostructures can be obtained with well defined electronic properties, i.e. either semiconductor or metallic, which may help to control the field emission properties. In addition, the oxides emitters can be operated in the presence of oxygen. These factors guaranteed a predictable voltage-current characteristic from nanostructured metal oxide field emitters. In most cases, aligned nanowire/nanotube films were measured using a diode-type field emission setup. There are no obvious differences in the field emission properties of nanowires, nanotubes and nanobelts. Typically, the linearity of $F-N$ plots from wide band-gap metal oxide nanowires is much better than that of

CHAPTER I Introduction

CNTs. Although many kinds of nanowires have shown more linear $F-N$ plots, the non-linearity or multi-region linearity was still observed in high electric field ranges.¹⁵ The reason could be attributed to gradual turn-on process of different morphological emitters which is different from that of CNTs. Among different morphological manifestations of the same material, one with sharper tip and higher aspect ratio was found to exhibit better field emitting characteristics. Some important milestones in metal oxide field emission history will be introduced as follows.

It was not until 2002, that electron FE properties of ZnO nanowire films were investigated for the first time. Many efforts have been made to investigate the emission mechanism and improve the emission performance of these nanostructures, including the experimental and theoretical exploration of FE process from individual metal oxide nanostructure emitters,^{141, 142} and the modification in electrical and morphological properties of these nanostructure emitter arrays by doping and plasma etching treatment.^{98, 101} As mentioned above, Lee and his co-workers¹⁴³ studied the FE properties of vertically well-aligned ZnO nanowires on the n -type Si substrate in 2002. The emission behavior of these nanowires is in accordance with $F-N$ theory. After that, the investigations on the FE properties of nanostructures expanded to other metal oxide nanomaterials, such as MoO₂, MoO₃, WO₃, CuO, Fe₂O₃ and so on.^{55, 106, 144-146} With the progress in nanostructure synthesis and device fabrication, Zhou *et al.*¹⁴⁵ developed one kind of FE display (FED) device consisting of indium tin oxide (ITO) glass coated with phosphor dyes as transparent anode plate and quasi-aligned tungsten oxide nanotip arrays as cathode in 2005. The Charge-Coupled Device (CCD) camera image indicates that uniform spatial distribution of emission sites can be driven by the suitable electrical field between two electrodes. Furthermore, Chen *et al.*¹⁰⁶ proposed a new FED device structure with double gates and corresponding driving method in 2007. WO₃ nanowires were employed as emitters. Not only still Arabic numerals and Chinese characters but also moving images could be clearly displayed by this device. The FE performance of this multiple pixel matrix FED is very close to that of the commercial metal emitter. (Fig. 1.18) For these 1D and Q1D metal oxide nanostructures, the turn on field reaches several volts per micrometer and the

CHAPTER I Introduction

emission current density varies from several micro-amperes per centimeter square to several tens of milliamperes per centimeter square, which can satisfy the requirements for industrial application. (10 mA/cm² current density is the minimum current density for industry applications.)

Figure 1.18 The progress road map of FE study on metal oxide nanostructures^{106, 143,}

145

Some significant FE results for different kinds of metal oxide nanostructure films are summarized in table 1.1.

CHAPTER I Introduction

Table 1.1 Important FE performance parameters and work function of several metal oxide semiconductor nanostructures reported in the literature.

Material	Morphology	Work function /eV	Synthesis method	Turn-on field / V/ μm (at 0.1 mA/cm ²)	Field-enhancement factor (β)	Ref.
Indium tin oxide (ITO)	Nanorods	4.7	Carbon thermal reduction	10	1140	147
IrO ₂	Nanorods	4.23	MOCVD	5.6	40000 $\pm$ 8000	148
RuO ₂	Nanorods	4.87	MOCVD	10.3	1153	149
MoO ₂	Nanorods	4.2	Thermal evaporation	4	N. A.	150
ZnO	Nanowires	5.3	CVD	6	847	143
CuO	Nanowires	2.5-2.8	Heat-Oxide	3.5-4.5	1570, 670	76
MoO ₃	Nanowires	4.6	Thermal evaporation	3.5	N. A.	151
In ₂ O ₃	Nanowires	5	CVD	7(aligned) and 10.7 (random)	N. A.	152
WO ₃	Nanowires	4.4	Thermal evaporation	13.85	N. A.	153
W ₁₈ O ₄₉	Nanotips	5.7	Thermal evaporation	10	N. A.	145
ZnO	Nanoneedle	5.4	Vapor phase deposition	2.4	2.3 $\times$ 10 ⁶	154
MoO ₃	Nanobelts	4.6	Heat-Oxide	6	450	155
Fe ₂ O ₃	Nanoflakes	5.4	Heat-Oxide	7.2	1131	77
Co ₃ O ₄	Nanowalls	4.5	CVD	5	302 $\pm$ 19; 1118 $\pm$ 41	74
ZnO	Tetrapod-like nanocrystal	5.4	Thermal evaporation	1.6	6285	156

The screening effect is dependent on the areal density of the emitter arrays. Evidently, the local electric field at the emitter tips is affected by its neighboring emitters. This screening effect is a determining factor of the emission characteristics. Thus the screening effect factor ranges from 0 for a densely packed emitter array to 1 for a single emitter.¹⁵⁷ For this reason, it is necessary to verify the field emission properties of the individual nanostructures avoiding the screening effect. Among all

CHAPTER I Introduction

FE research reports of the metal oxide nanostructures, only a few studies focus on the individual nanostructures, and most parts of them are concentrated on the individual ZnO nanostructure.^{141, 158-165} For example, Huang and his co-workers¹⁴² reported their study on the FE properties of pure and Indium (In) doped individual ZnO nanowire. Fig. 1.19 (a) shows the experimental setup of individual nanowire FE testing by an *in situ* TEM method using a home-made piezo-manipulator. Although these two types of nanowires have similar morphology (Fig. 1.19 (b) and (c)), the experimental results show that In-doped ZnO nanowires have an enhanced FE performance. The turn on field E_{to} (defined the electric field by the emission current of 0.1 μA for a single nanowire emitter) are found to be about 228 and 193 $\text{V}/\mu\text{m}$ for pure and In-doped ZnO nanowires, respectively. (Fig. 1.20 (a)) On the basis of the above, In-doped ZnO nanowire shows a much lower E_{to} than that of pure ones. The $F-N$ plot of pure nanowire can be easily fitted into a straight line, but that of In-doped one only can be fitted to two straight lines, corresponding to the proposed two-band mode FE mechanism. (Fig. 1.20 (b))

Figure 1.19 (a) Setup of the *in situ* measurement. (b) A single pure ZnO nanowire with a diameter of approximately 100 nm and (c) In-doped ZnO nanowire with a diameter of approximately 100 nm used in FE measurement.¹⁴²

CHAPTER I Introduction

Figure 1.20 (a) *I-V* curves and (b) the corresponding *F-N* plots for a single In-doped ZnO nanowire and pure one, respectively. The lines in the *F-N* plots are the linear fit of the experimental curves.¹⁴²

Some significant evaluating indicators of FE properties for these individual metal oxide nano-emitters are summarized in table 1.2

Table 1.2 Important evaluating indicators of FE properties for individual metal oxide nano-emitters

Material	Morphology	Work function /eV	Synthesis method	Turn-on voltage / V (at 100 nA)	Field-enhancement factor (β)	Ref.
ZnO	Nanowire	5.3	CVD	348	1110	141
In doped ZnO	Nanowire	1.70	CVD	290	48.4	142

FE properties of individual nanostructures are mainly dependent on the intrinsic and extrinsic properties for identified materials. In order to achieve higher emission current and lower turn on field, research expanded from ZnO nanowire to other 1D and Q1D metal oxide nanomaterials. To address this issue, individual single-crystalline PTB nanowire is chosen for investigation in this Ph.D project, due

CHAPTER I Introduction

to its low work function 1.76 eV¹⁶⁶ and metallic electrical transport properties, which could enhance its FE performance. Detailed results and discussions will be introduced in Chapter V.

Although tremendous progress on FE research of metal oxide nanostructures have already been made, there are still huge challenges to fabricate and characterize appropriate 1D and Q1D metal oxide nano-emitters. These challenges will excite and motivate material and physical scientists to carry out intensive study in future.

1.4 Motivation and objectives

From the reviews presented above, many results have been achieved for the growth and FE properties of 1D and Q1D metal oxide nanostructures. Nonetheless, most works adopted high temperature synthesis processes and are limited to using a CVD system with precise control on gas flow. Although the morphology and chemical composition of nanostructures in these growth processes can be accurately adjusted, the composition ratio of gas mixture and gas flow rate, even the locations of the source material and substrate need to be carefully controlled. So it is important to explore novel fabrication methods with mass production potential, rapid growth, catalyst-free, diversity of materials made, low-formation temperature, and reasonably low costs. Heat-Oxide method, as a new synthetic method, has been shown to provide an alternative route for fabrication of metal oxide nanostructures, with the advantages of mild synthetic conditions, simple manipulation, and large-scale production.⁷⁴ However, there still remains a large number of blanks which need to be filled in this fabrication method. Firstly, the exact growth mechanisms of some metal oxide nanostructures remain unclear for this synthetic method which certainly weakens the control effect during the growth process. Secondly, for the point view of materials, it is still a difficult problem to directly fabricate metal oxide nanostructures with controllable doping elements. It is a nice attempt to employ this Heat-Oxide method to simplify the doping process, although the doping profile needs further

CHAPTER I Introduction

improvement.

As introduced in Section 1.3, the study on FE property is also one of the motivations in fabricating 1D and Q1D metal oxide nanostructures. It is necessary to understand the detailed FE mechanism, find out the optimized testing parameters and conditions, and thus improve the FE performance of nanostructures. The key influencing factors affecting the FE properties of nanostructure arrays are morphology effect and screening effect. The morphology of metal oxide nanostructures is dominant factor of their FE process. Until now many methods have been adapted to affect this factor. Reactive ion etching (RIE) is the conventional method to modify the extrinsic properties of these nanostructures after the synthesis step. Argon (Ar) plasma generated by RIE system, as one kind of clean and non-toxic gas plasma, can be widely used in research and industrial field. Its influence on the surface morphology of metal oxide nanostructures for improving FE performance has rarely been addressed. The shielding effect or screening effect is another influencing factor which occurs on a subatomic level between electrons occupying energy levels and is caused by repulsive forces of other electrons between it and the nucleus. For field emitters array, the geometry effect embodies the structure morphology and the screening effect embodies the density of the nanostructures. The study results on the FE properties of individual nanostructure may easily avoid this shielding effect.

In this thesis, we will work on several novel types of α -Fe₂O₃ and PTB and focus on the following objectives:

1. The synthesis and growth mechanism of α -Fe₂O₃ nanoflakes and PTB nanostructures.
2. The FE properties of ultra-sharp α -Fe₂O₃ nanoflake films and PTB nanowire films. Moreover, further FE enhancement of α -Fe₂O₃ nanoflake films by employing RIE argon plasma treatment.
3. Polarization micro-Raman study and electrical transport properties of individual PTB K_{0.33}W_{0.94}O₃ nanowire, which may show influence of the potassium element doping in the WO₃ crystal lattice.
4. The FE properties of individual PTB nanowire with anode geometrical effects and

CHAPTER I Introduction

gate potential effects. Because the ultrasonic machine will be employed in distribution step of the individual nano-emitter experiments, we can not investigate the FE process of the individual α -Fe₂O₃ nanoflake due to its frangibility. We will only focus on the individual PTB nanowires.

We will further extend the Heat-Oxide synthesis method to fabricate other kinds of metal oxide materials such as MoO₃ and In₂O₃. In this project, we will further try to extend the Heat-Oxide method in a three-zone tube furnace and on a high temperature hot plate to synthesize various functional metal oxide nanostructures for practical applications. We will try the sol-gel and hydrothermal methods for the same motivation. However, the results of this part are embodied in the collaboration works with other researchers which will not be included in this thesis.

1.5 Organization of this thesis

This thesis is divided into 6 chapters and their contents are briefly described below.

Chapter I introduces the background of this research, including the classification of metal oxide nanostructures, the growth, the properties and the applications of 1D and Q1D metal oxide nanostructures. Field electron emission, as one of their applications, is detailed in this chapter. The current research status and future development of the FE theory are also summarized.

Chapter II presents the fabrication, modification and measurement techniques used for α -Fe₂O₃ nanoflakes and PTB nanowires. Firstly, the sample preparation method of α -Fe₂O₃ nanoflakes and PTB nanowire, followed by the fabrication of PTB nanowire FET devices are discussed. Secondly, the measurement setup and techniques used to characterize transport properties of individual nanowire FET device are described. Later on, the reactive ion etching (RIE) modification method and its mechanism will be introduced. Finally, the experimental setup for film samples and individual nanowire sample are illustrated, respectively.

CHAPTER I Introduction

Chapter III focuses on the growth of the α -Fe₂O₃ nanoflake films with different growth conditions and their FE properties. The effect of the morphology influencing the FE properties is symmetrically studied. The different morphologies of the nanoflake are determined by the growth temperatures. Argon gas plasma treatment is employed and the detailed mechanism of this kind enhancement is investigated.

Chapter IV introduces the synthesis and characterization of the novel PTB nanostructure films. The FE measurement and emission current stability test are performed. The electrical transport property of the individual PTB nanowire devices is investigated and metallic property is observed. The Raman imaging and orientation dependent Raman spectra were also carried.

In Chapter V, FE properties on individual PTB nanowire are systemically investigated. The effect of electrostatic gating and electrodes geometrics are examined. By setting the measurement geometrical environment as a boundary condition, we also calculate the electric field distributions and the finite element simulation results support our experimental results.

Chapter VI summarizes our research contributions on the α -Fe₂O₃ nanoflakes and PTB nanostructures. And it also points out our some future research proposals in this area.

CHAPTER II Experimental Details

CHAPTER II EXPERIMENTAL DETAILS

This chapter presents fabrication, modification and characterization techniques used for α -Fe₂O₃ nanoflakes and potassium tungsten bronze (PTB) nanostructures. Firstly, we describe the preparation of α -Fe₂O₃ nanoflakes and PTB nanostructures, respectively. And then the fabrication of PTB nanowire field effect transistor (FET) devices is introduced. Secondly, the experimental setup and technique used to characterize electrical transport properties of nanowire FET are discussed. Later on, the reactive ion etching (RIE) process and mechanism are investigated. Its influence on enhancing the FE performance of α -Fe₂O₃ nanoflakes is systemically studied. Finally, the FE setups for film samples and individual nanowire sample are discussed, respectively.

2.1 Sample preparation and device fabrication

2.1.1 Sample preparation

The growth methods and mechanism of 1D and Q1D metal oxide nanostructures have been in general introduced in Chapter I. Although large scale α -Fe₂O₃ nanoflake samples have been successfully synthesized, the challenge on fabricating a film specimen appropriating for large area FE applications still exists.

Following the same Heat-Oxide synthesis procedure¹⁸ mentioned in Section 1.2.3, we further expand the heating temperatures for fabricating α -Fe₂O₃ nanoflakes into the range of 260 – 400 °C. Experimentally, fresh iron foils (10 mm × 10 mm × 0.25 mm) with a purity of 99.9% (Aldrich) are used as both reagents and substrates for the growth of α -Fe₂O₃ nanoflakes. After rinsing by deionized water, the cleaned Fe foil is heated on a hotplate under ambient conditions. The growth temperatures vary from

CHAPTER II Experimental Details

260 °C to 400 °C and the growth duration is fixed as 10 hours. It is found that the temperature parameters strongly affect the growth processes and the final morphologies of the α -Fe₂O₃ nanoflakes. The ultra-sharp nanoflake film samples synthesized at 260 °C, exhibit promising electron FE properties in a large scale. The detailed results and discussion will be carried out in Chapter III.

According to similar synthesis method, the PTB nanostructures, including nanowires and nanosheets, are successfully fabricated by this method. The experiment procedure is described below. Fresh tungsten foils (10 mm × 10 mm × 0.25 mm) with a purity of 99.9% (Aldrich) are used as both reagents and substrates for the growth of PTB nanostructures. After having been polished and cleaned, tungsten foils are sonicated in the potassium hydroxide solution (0.01 mol/dm³). Then, the tungsten foil is heated on a hotplate under ambient conditions after it dries naturally. The growth temperature varies from 450 to 600 °C and the duration is fixed at 10 hours. In our experiment, the influential factors on the growth of PTB nanostructures, such as temperature and reaction time, will be discussed in Chapter IV.

2.1.2 Device fabrication

After the fabrication of PTB nanowires, the individual nanowire back-gate FET is fabricated on SiO₂/Si (i.e. 200 nm insulated SiO₂ film over heavily doped Si wafer) substrate. Firstly, the as-grown PTB nanowires are dispersed into deionized water by ultrasonication. The nanowire suspension is then dropped on SiO₂/Si substrate. A layer of SU-8 photoresist is subsequently spun over the substrate. Two electrical contact pad patterns are exposed by UV lithography. After the development, a 100 nm thick Au film is deposited over the structure by Radio Frequency (RF) sputtering deposition and followed by a lift-off process. The schematic diagram of configuration and optical image of a single PTB nanowire FET are shown in Fig. 2.1 (a) and (b), respectively.

CHAPTER II Experimental Details

Figure 2.1 (a) Schematic diagram of a single PTB nanowire FET configuration with basic electrical setup. (b) Optical image of the FET.

2.2 Electrical transport measurement setup

Electrical transport property is an important physical property of 1D and Q1D nanostructures because they are the best choice as a building block of nanoscale electro-devices.¹⁰⁹ Normally metal oxide nanomaterials behave like semiconductors or insulators,^{110, 167, 168} while their metallic property is scarcely reported. 1D metallic nanostructures can work as electrical interconnects or nanoelectrodes. In this thesis, we report the DC electrical transport properties of PTB $K_{0.33}W_{0.944}O_3$ nanowire for the first time.

The devices fabrication process has been introduced in section 2.1. Optical image of an individual FET is shown in Fig. 2.1 (b). The length of the channel between two electrodes is around 5 μm and the diameter of the nanowire is around 100 nm. The basic measurement setup in our investigation is shown in Fig. 2.2. The gate voltage was applied on the heavily doped Si wafer employed as the back gate electrode. The electrical transport properties were measured on a Karl Suss probe station with a Keithley 4200 SCS (semiconductor characterization system) in air at room temperature (Fig. 2.2). In case of transport measurement, two-point electrical measurements are carried out using tungsten tips. These tips coupled with a DC voltage from Keithley 4200 output and the current across the sample is measured by

CHAPTER II Experimental Details

the same semiconductor parameter analyzer simultaneously. The back gate bias is applied while the DC measurement is carried out. We will discuss the detailed results in Chapter IV.

Figure 2.2 (a) Keithley 4200 SCS (semiconductor characterization system). (b) Karl Suss probe station

2.3 Reactive Ion Etching (RIE) and plasma bombardment treatment

Typical reactive ion etching (RIE) system consists of a low pressure vacuum chamber equipped with two parallel plates as the electrodes. The chemically reactive plasma is generated from different gas sources in the chamber by applying a strong radio frequency (RF) electromagnetic field between these two plates. The high energy ions and gas molecular initiated by hundred watts and 13.56 MHz AC field will attack the surface of samples and react with it. The schematic diagram is shown in Fig. 2.3. This etching technique is usually used to remove surface material deposited on wafers.

CHAPTER II Experimental Details

Figure 2.3 A schematic diagram of RIE system.

The effects of H_2 , Ar, O_2 and CF_4 plasmas adopted to modify 1D metal oxide nanostructures have been introduced in Section 1.2.4. Plasma treatment is regarded as a simple and efficient method to improve the FE performance of nanostructures.⁹⁹⁻¹⁰¹ Argon (Ar) plasma is one kind of clean and non-toxic gas plasmas, which can be widely used in research and industrial field. Although there are a plenty of publications focusing on Ar plasma treatment for enhancing FE properties of carbon nanotube (CNT) films,^{169, 170} its mechanisms of improving FE performance of metal oxide nanostructures have rarely been addressed in the literatures.¹⁷¹ Its influence on the surface crystal structures is totally different from its influence on CNT. In this thesis, Ar plasma treatment in the improvement of FE performance on ultra-sharp $\alpha\text{-Fe}_2\text{O}_3$ nanoflakes is systemically studied. The experiment procedure is described below.

The growth temperature is fixed at 260 °C for producing ultra-sharp $\alpha\text{-Fe}_2\text{O}_3$ nanoflakes. And the heating duration is 15 hours. The plasma treatment was

CHAPTER II Experimental Details

conducted by a plasma etching system (March PX-250) under the following conditions: radio-frequency (RF) frequency of 13.56 MHz, flow rate of 20 *sccm*, operating pressure of 0.2 Torr, RF power of 100 W, D. C. bias of 220 V and process duration of 10 min. The detail results and discussion will be presented in Chapter III.

2.4 Field emission experimental setup

The unique structure of 1D and Q1D metal oxide nanostructures indicates they are ideal systems for producing high FE current-density devices. We will introduce the experimental setups for FE testing, including film sample and individual nanowire sample in next two sections, respectively.

2.4.1 Field emission setup of nanostructure film

The two-parallel-plate FE measurement configuration of film samples is schematically shown in Fig. 2.4. In a vacuum chamber with a base pressure of about 5.8×10^{-7} Torr at room temperature, the whole nanostructure film is mounted onto a steel plate as the cathode and indium-tin oxide (ITO) glass is employed as the anode to collect field emitted electrons. A insulated Polyethylene terephthalate (PET) transparency film with a thickness of 100 μm and a hollow of 0.04 cm^2 area is employed as a spacer and utilized to define the gap between electrodes and to cover the whole support platform of film sample simultaneously. Thus, only those nanostructures in the hollow area are exposed for FE study. Details of the measurement result and analysis are reported in Section 3.4.⁷⁶

CHAPTER II Experimental Details

Figure 2.4 Schematic of film sample FE test system setup.

2.4.2 Field emission setup of individual nanowire

Single crystalline PTB $\text{K}_{0.33}\text{W}_{0.944}\text{O}_3$ nanowires¹⁷² have been produced by Heat-Oxide method mentioned in Section 2.1. To understand the essential field induced emission behavior of individual PTB nanowire, it is desirable to perform FE measurements under the observation of scanning electron microscope (SEM) (JEOL JSM-6700F). The detailed setup is introduced as below.

First of all, the PTB nanowires are dispersed from the tungsten foil substrates into deionized water by 10 min ultrasonication for nanowire suspension. The dielectrophoresis (DEP) process and two-electrode diode type configuration are employed to assemble individual nanowire to electrochemically etched tungsten tip. Firstly, we apply a droplet of nanowire suspension onto CNT film as one electrode and then push etched tungsten tip as another electrode into this droplet carefully. (Fig. 2.5 (a)) After that, the two electrodes are coupled with an AC voltage source with amplitude of 10 V and frequency of 10 kHz, which is chosen for optimizing the attachment. (Fig. 2.5 (b)) This AC source generates an alternating electrostatic force between the nanowire and the tungsten tip in suspension.¹⁷³ By adjusting the concentration of nanowire suspension, it is possible that only a single nanowire is attached on the etched tip. (Fig. 2.5 (c))

CHAPTER II Experimental Details

Figure 2.5 (a) Optical image of the W tip into the suspension droplet on CNT film. (b) Illustration of the setup for attachment of PTB nanowires to an etched W tip using the dielectrophoresis effect. (c) SEM image of an individual PTB nanowire attached to the electrochemically etched W tip.

Unlike the typical two-flat-electrode configuration for film samples,⁷⁷ we employ the individual PTB nanowire as the cathode fixed on the copper specimen holder and another etched tungsten tip as the anode which can be precisely controlled by a piezodriven nanomanipulator (Kleindiek) in vacuum chamber. The third tungsten tip on another nanomanipulator coated with 100 nm thick SiO_2 layer is used as the single side gate electrode which is perpendicular to the emitters. (Fig. 2.6) The SiO_2 layer is deposited by pulsed laser deposition. The vacuum as the SEM cavity is 9.5×10^{-5} Pa. The electron beam is blanked off and the nanowire is discharged in advance before measurement.

An example of individually mounted PTB nanowire is shown in Fig. 2.6 (b), in which the electrical circuit, the morphology of the nanowire and the configuration of the measurement system, *i.e.*, the inter-electrode distance d , the length of nanowire l , the diameter of it w , the distance between gate electrode and emitter d' , are illustrated.

CHAPTER II Experimental Details

Figure 2.6 FE measurement apparatus and parameters. (a) Optical image of the experimental setup in SEM chamber. (b) The SEM image with schematic diagram of the experimental setup. The inset image shows the nanowire of the length l and diameter w with the sharp anode positioned at a distance d and the single-side-gate positioned at a distance d' .

The anode geometrical effects have been studied systematically:

- 1) Two types of anode morphology, such as flat plane (wire body) or needle tip (etched tip), have been applied to measure the FE of individual PTB nanowire.
- 2) The distance d between two electrodes can be adjusted from several to tens of micrometers. (Fig. 2.7 (a) and (b))
- 3) The angle α between the normal direction of the nanowire and the connection line of two electrodes can be adjusted from 0 to 75 degrees. (Fig. 2.7 (c))

The detailed results and analysis will be performed in Chapter V.

CHAPTER II Experimental Details

Figure 2.7 (a) and (b) SEM images showing typical experimental configuration and definition of distance d between two electrodes with flat plane anode setup and tip anode setup, respectively. (c) SEM image showing typical experimental configuration and definition of the angle α between two electrodes with tip anode setup.

CHAPTER III Synthesis and Characterization of α -Fe₂O₃ Nanoflakes and Their Field Emission Properties

CHAPTER III SYNTHESIS AND CHARACTERIZATION OF α -Fe₂O₃ NANOFLAKES AND THEIR FIELD EMISSION PROPERTIES

3.1 Introduction

This chapter focuses on the growth of α -Fe₂O₃ nanoflake films with different growth conditions and their field emission (FE) properties. It is proven by several characterization techniques that the different morphologies of nanoflakes are determined by the growth temperatures. Furthermore, in order to improve the FE performance of these nanoflake films, Argon gas plasma treatment is employed and the detailed enhancement mechanism is investigated.

3.2 Morphology and crystal structure

The morphologies of the as-prepared products are examined by scanning electron microscopy (SEM) (JEOL JSM-6700F) for topographical morphology; the compositions of the top surface are characterized by X-ray diffraction (XRD) (Bruker D8 with Cu K α irradiation) and micro-Raman spectroscopy (Witech CRM200, λ_{laser} =532 nm). Transmission electron microscopy (TEM) (JEOL JEM 2010F, 200 kV) is used to study the crystal structure of the ultra-sharp nanoflake products.

Fig. 3.1 shows the SEM images of the as-prepared samples obtained by heating iron foils on a hotplate with different temperatures (260 – 400 °C) and fixed duration (10 hours). Clearly, the flakes become broader with increasing reaction temperatures, indicating the obvious heating temperature's effect on the morphologies of the nanostructures. To further quantify this effect, the sharpness of the nanoflakes with

CHAPTER III Synthesis and Characterization of α -Fe₂O₃ Nanoflakes and Their Field Emission Properties

different growth temperatures are investigated based on high magnification SEM images. The sharpness of the nanoflake is measured by two ways in this work: one is the radius of curvature at the nanoflake tip and the other is the aspect ratio of L/FWHL (L is the length of nanoflake and FWHL is the full width of the half length). As shown in Fig. 3.2, the lower heating temperature dramatically increases the sharpness of flakes as indicated by the higher aspect ratio and smaller radius. In general, the randomly aligned nanoflakes synthesized at the lowest temperature, 260 °C are about 5-10 nm in thickness, 20 nm at the base, 5 nm at the tip and 1-2 μ m in length. Comparing with the flakes formed at 300 °C (24 hours),¹⁸ the nanoflakes synthesized in this work show an ultra-sharp needle-like shape and a lower density which may effectively enhance the field induced electron emission from such nanoflake film.

Figure 3.1 SEM images of the top surfaces of iron foils heated for 10 hours at (a) 260 °C, (b) 300 °C, (c) 350 °C and (d) 400 °C.

CHAPTER III Synthesis and Characterization of α -Fe₂O₃ Nanoflakes and Their Field Emission Properties

Figure 3.2 (a) (a1 - a4) High magnification SEM images of the nanoflakes synthesized at 260, 300, 350, and 400 °C, respectively. (b) Aspect ratio (solid squares) defined as length over full width at half length and radii (solid circles) of tangent circles of the tips as a function of heating temperatures.

Fig. 3.3 (a) shows XRD pattern of one as-prepared sample. Two phases of iron oxide, α -Fe₂O₃ and Fe₃O₄ were formed by heating Fe foil in air at 260 °C. The peaks corresponding to the rhombohedral α -Fe₂O₃ with lattice constants $a = 5.035$ Å and $c = 13.749$ Å are readily confirmed from XRD pattern.¹⁷⁴ It was also noted that, comparing with the standard powder diffraction pattern of bulk α -Fe₂O₃, our XRD pattern of the α -Fe₂O₃ nanoflakes exhibits a much higher ratio of the intensity of the (110) planes' diffraction peak to the intensity of the (104) planes' (2.5, nanoflakes vs 0.76, powder¹⁷⁴). This may indicate the existence of a favorable growth plane, as

CHAPTER III Synthesis and Characterization of α -Fe₂O₃ Nanoflakes and Their Field Emission Properties

evidenced by our TEM results discussed below. The Raman spectrum of the top surface of the as-prepared sample is shown in Figure 3.3 (b). Seven peaks are presented in the range of 150 – 800 cm⁻¹. The peaks located at 225, 245, 291, 408 and 499 cm⁻¹ correspond to the α -Fe₂O₃ phase,¹⁷⁵ namely two A_{1g} modes (225 and 499 cm⁻¹) and three E_g modes (245, 291 and 408 cm⁻¹). Those peaks located at 552 and 671 cm⁻¹ correspond to Fe₃O₄,¹⁷⁶ namely T_{2g} mode (552 cm⁻¹) and A_{1g} mode (671 cm⁻¹).

Figure 3.3 (a) XRD pattern and (b) Raman spectrum of the as-prepared sample shown in Fig. 2.2 (a).

The TEM is employed to further confirm the composition and the crystal structure of the ultra-sharp nanoflakes. Fig. 3.4 (a) shows the typical TEM image of α -Fe₂O₃

CHAPTER III Synthesis and Characterization of α -Fe₂O₃ Nanoflakes and Their Field Emission Properties

nanoflake. As seen in Fig. 3.4 (b), high resolution TEM (HRTEM) image is taken in the region circled in Fig. 3.4 (a). The fringe spacing of 0.252 nm concurs well with the interplanar spacing of the plane (110)¹⁷⁴. Its corresponding selected area electron diffraction (SAED) pattern of the flake is shown in Fig. 3.4 (c). The growth direction of the nanoflakes is [110], which is consistent with our previous study.¹⁵

Figure 3.4 (a) TEM image of the α -Fe₂O₃ nanoflakes, (b) HRTEM image of the nanoflakes and (c) the electron diffraction pattern (circled region) of nanoflakes showing good agreement with the diffraction pattern of α -Fe₂O₃ from the zone axis of $[\bar{4}41]$.

According to these characterization results of as-grown nanostructures synthesized at different growth temperatures, we deduce the growth mechanism of these nanoflakes in the following section.

3.3 Growth mechanism of α -Fe₂O₃ nanoflakes

As described in Section 1.2.3, fresh iron foils are heated directly on a hotplate with the temperature range of 260 – 400 °C under ambient conditions. α -Fe₂O₃ nanoflakes with different morphologies are successfully synthesized. The detailed growth

CHAPTER III Synthesis and Characterization of α -Fe₂O₃ Nanoflakes and Their Field Emission Properties

mechanism will be discussed below.

Because the growth temperatures in this process are much lower than the melting points of Fe and α -Fe₂O₃ (1535 and 1350 °C, respectively),³⁷ the growth of α -Fe₂O₃ nanoflakes is inexplicable by the vapor phase mechanism such as the Vapor-Liquid-Solid (VLS) and Vapor-Solid (VS) processes.³¹ In this work, we attribute the growth mechanism to the surface diffusion of iron atoms and iron oxide molecules. A schematic view of the formation of α -Fe₂O₃ nanoflakes is shown in Fig. 3.5. Initially, the top layer of iron foil is oxidized by the oxygen molecules in air and formed a very thin layer of mixture of α -Fe₂O₃ and Fe₃O₄, which can be observed and determined by cross-section SEM and Raman spectroscopy.¹⁷⁷ (The SEM image and Raman spectrum did not show here) With continuous heating, the Fe₃O₄ at the very top layer is further oxidized to α -Fe₂O₃ and another layer of Fe₃O₄ below the thin top layer of α -Fe₂O₃ is formed by the reaction between oxygen diffusing through the thin top layer and iron substrate. During the formation and growth of the α -Fe₂O₃ layer, substantial stresses are expected to accumulate. Once a critical limit is reached, the stresses are relaxed by slipping in α -Fe₂O₃ crystals and screw dislocations might be produced. When the dislocations are generated along an appropriate crystal direction, iron atoms and iron oxide molecules adsorbed on the surface begin to migrate toward and stack in the corresponding plane to maintain a flake shape.¹⁷⁸ The preferential migration crystal direction, especially at the lower heating temperatures (for example, 260 °C), may be [110] and the growth plane may be (110) where the oxygen is rich and Fe is deficient in the crystal lattice of α -Fe₂O₃.³¹ Driven by the O-richness and Fe-deficiency, at low temperatures (260 – 300 °C), the diffusion of iron atoms and oxide molecules along the [110] direction is more facile so that the growth is mainly along the [110] direction named as the axis growth,¹⁷⁸ which resulted in the large aspect ratio (> 40) shown in Fig. 3.1 (b). At higher temperatures (350 – 400 °C), the diffusion in other crystal directions may be enhanced and radial growth occurs. This resulted in the broadening of nanoflakes and small aspect ratio (≤ 10). It is concluded that the morphologies of α -Fe₂O₃ nanostructures can be reasonably controlled by

CHAPTER III Synthesis and Characterization of α -Fe₂O₃ Nanoflakes and Their Field Emission Properties

varying the reaction temperature of Heat-Oxide method. In other words, the lower temperature supports the sharp nanoflake growth, whereas broad nanoflakes are grown at the higher temperature. The length to width aspect ratio of nanoflake has a direct influence towards its FE properties, which will be discussed in next section.

Figure 3.5 A schematic diagram of the α -Fe₂O₃ nanoflake growth process.

3.4 Field emission from α -Fe₂O₃ nanoflake films

The study of FE is one of the motivations in fabricating 1D and Q1D nanostructured α -Fe₂O₃ in the current research.¹⁵ Considering the ultra-sharp morphology of α -Fe₂O₃ nanoflakes synthesized at low temperature of 260 °C, we study their FE properties as film samples. Fig. 3.6 shows the typical current density–electric voltage (J – V) curve. It is found that the emission current and the applied field exhibits exponential dependence relationship which is plotted as a $\ln(J/E^2) \sim 1/E$ inset in Fig. 3.6. The results indicate that FE behavior of α -Fe₂O₃ ultra-sharp nanoflake films follows the F – N relationship.¹²³ The experimental data can be fitted by the simplified F – N equation (1.5) which has been mentioned in Section 1.3.3. The dots are the emission current data the red solid line is the corresponding fit

CHAPTER III Synthesis and Characterization of α -Fe₂O₃ Nanoflakes and Their Field Emission Properties

curve (Fig. 3.6). For α -Fe₂O₃, the work function ϕ is assumed to be 5.4 eV.¹⁷⁹ Here, β is the field enhancement factor, which is defined by:

$$E_{local} = \beta E = \beta \frac{V}{d} \quad (1.12)$$

where E_{local} is the local electric field near the emitter tip, d is the average spacing between the electrodes ($d = 100 \mu\text{m}$ in this work) and V is the applied voltage. For the α -Fe₂O₃ ultra-sharp nanoflakes with the lowest growth temperature (260 °C), β was obtained to be 1131 from the linear fitting of the F - N curve and the turn-on field was measured to be about 7.2 V/ μm (Fig. 3.6). Compared to the AlN nanoneedles ($\beta = 950$),¹²⁶ NiSi₂ nanorods ($\beta = 630$),¹⁸⁰ TiSi₂ nanowires ($\beta = 501$)¹⁸¹ and the α -Fe₂O₃ nanowires ($\beta = 560$ and 1500),¹⁸² such an enhancement factor is acceptable for application, although the value is much lower than that of carbon nanotubes.¹⁸³ One of possible reasons could be the random alignment of the nanoflakes (Fig. 3.1 (a)). We can also see that at high electric fields the linear relationship between $\ln(J/E^2)$ and $1/E$ suggests that the quantum tunneling mechanism is responsible for the emission from the ultra-sharp nanoflakes.¹⁸⁴ In early works,^{15, 18} the electron FE is only effectively observed from the α -Fe₂O₃ nanoflakes grown on atomic force microscope (AFM) tips or tungsten tips but not from the film. That is because the curvature of the tip apex will enhance the FE properties for broad nanoflakes which are grown at the high temperature (≥ 300 °C). In this work, ultra-sharp α -Fe₂O₃ nanoflake films with a large scale exhibit promising FE properties. This improvement may be because of the ultra-sharp morphology and a lower density which are able to effectively weaken the screening effect, and increase the field enhancement factor^{76, 145} (shown in Fig. 3.1) and consequently enhance the FE efficiency.

CHAPTER III Synthesis and Characterization of α -Fe₂O₃ Nanoflakes and Their Field Emission Properties

Figure 3.6 Typical field-emission current density–voltage (J – V) curves of the α -Fe₂O₃ nanoflakes films synthesized at 260 °C for 10 hours. Inset shows the F – N plots ($\ln(J/E^2)$ vs. $1/E$) accordingly, which exhibits a good linear dependence (solid line is the fitting result).

3.5 Plasma bombardment treated α -Fe₂O₃ nanoflakes

Practically, high current density and low turn-on field are the most desirable properties for electron emitters. For a given material, FE properties are mainly dependent on the morphologies like dimension and apex geometry of 1D and Q1D nanostructures. To improve the FE properties of nanostructures, several methods are employed before and after the synthesis process, for example, increasing the carrier concentration by heavy ion doping¹⁸⁵ or modifying the apex geometry by gas plasma treatment.¹⁰¹ Here, Argon gas plasma generated by RIE system is employed to bombard and modify the surface crystal structures of ultra-sharp α -Fe₂O₃ nanoflake. There will be no chemical reaction between α -Fe₂O₃ nanoflake and Argon molecular and ions according the chemical durability of Argon. The experimental details have been discussed in Section 1.2.4.

CHAPTER III Synthesis and Characterization of α -Fe₂O₃ Nanoflakes and Their Field Emission Properties

3.5.1 Modification of crystal structure

The XRD patterns and Raman spectra are taken before and after plasma treatment, and the results shown in Fig. 3.7 can be used to illustrate the influence of the plasma treatment on the film samples. The influences of Ar plasma treatment on the morphology and surface crystal structure of α -Fe₂O₃ nanoflakes need to be further confirmed by other characterization methods.

Figure 3.7 (a) XRD patterns and (b) Raman spectra of the as-prepared sample and Ar plasma treated samples.

CHAPTER III Synthesis and Characterization of α -Fe₂O₃ Nanoflakes and Their Field Emission Properties

To further reveal the influence of the Ar plasma treatment on the structure of the surface and interior of the nanoflakes at an atomic level, TEM observation is employed. Fig. 3.8 displays the representative TEM images of α -Fe₂O₃ nanoflakes before and after Ar plasma treatment for 10 min. As can be seen in Fig. 3.8 (b), a very thin amorphous layer covers the surface of the as-grown nanoflakes, which is shown between two solid black lines. A typical low magnification TEM image of the plasma-treated nanoflakes is shown in Fig. 3.8 (c). It is obvious that the amorphous layer has been totally removed by Ar plasma and the surface of nanoflakes becomes clean on atomic scale. More importantly, plenty of surface protrusions as indicated by the arrows are formed by plasma treatment (Inset of Fig. 3.8 (c)). The extension of the crystal lattice readily demonstrates that such protrusions of 1–3 nm in size are epitaxially connected with the original round tip body. Considering the XRD, Raman and TEM results, the main effect of Ar plasma in this work is removing the amorphous layer and creating nano-protrusions. The projected structure can be seen through a bright-field TEM image of one α -Fe₂O₃ nanoflake (Fig. 3.9 (a)). The corresponding dark-field TEM further confirms the existence of the protrusions on the surface of plasma-treated nanoflakes (Fig. 3.9 (b)).

CHAPTER III Synthesis and Characterization of α -Fe₂O₃ Nanoflakes and Their Field Emission Properties

Figure 3.8 (a) TEM image of the α -Fe₂O₃ nanoflake before plasma treated, (b) High resolution TEM image of (a), (c) TEM image of the α -Fe₂O₃ nanoflake after plasma treatment. Inset of (c) shows the high resolution TEM image the highlighted part.

CHAPTER III Synthesis and Characterization of α -Fe₂O₃ Nanoflakes and Their Field Emission Properties

Figure 3.9 (a) Dark-field and (b) bright-field TEM images of the tip of the α -Fe₂O₃ nanoflake after plasma treatment.

3.5.2 Field emission enhancement

Fig. 3.10 (a) plots the typical current density – electric field (J – E) curves of the nanoflakes before and after Ar plasma treatment. The as-grown and post-treatment nanoflakes exhibit significantly different emission behaviors. Detailed measurements reveal that the electron emission performance of the plasma-treated samples has been dramatically improved. For example, the maximum current density (under the field of 11 V/ μ m) has been increased from the original 16 μ A/cm² to 60 μ A/cm². At the same time, E_{10} has been reduced from 10 V/ μ m to 8 V/ μ m after 10 min exposure to Ar plasma. The exponential dependence between the emission current and the applied field, plotted by the $\ln(J/E^2) \sim 1/E$ relationship (inset of Fig. 3.10 (a)) are found for both the as-grown and the plasma-treated samples. Field enhancement factor β , as the

CHAPTER III Synthesis and Characterization of α -Fe₂O₃ Nanoflakes and Their Field Emission Properties

parameter depending on the aspect ratio of the nanostructures, crystal structures and the density of the emitting points, is obtained to be 1131 from the linear fitting of the $F-N$ curve at turn-on area while that of Ar plasma treated nanoflakes is 3218. Based on the results of morphological and crystal structural investigations (Fig. 3.8 and 3.9), we could draw some conclusion on the enhancement of FE performance by Ar plasma treatment:

- 1). The plasma etching process effectively removes the amorphous coating and cleans the nanoflakes at atomic level.
- 2). Ultra-sharp sub-tips of 1-3 nm could be created by the plasma treatment which can remarkable reduce the diameter of the emitter for increasing the field enhancement factor.¹²⁶
- 3). The density of emitters is significantly increased.

All these effects could enhance the factor β and consequently improve the emission performance.

The FE stability of the plasma-treated α -Fe₂O₃ nanoflake film samples are investigated and the most typical result is shown in Fig. 3.10 (b). The total emission current is monitored over 30 min under an applied macroscopic field of 9 V/ μ m and an emitter – anode gap of 100 μ m. At an average emission current density of $\sim 7 \mu\text{A}/\text{cm}^2$, their fluctuations were less than 5 % and no oblivious degradation was observed in all testing samples. Comparing with our previous results,¹⁸ it is believed that the Ar plasma treatment will not only improve the current density but also extend the stability of the FE current. These results reveal the possibility of Ar plasma treatment to improve the FE performance.

CHAPTER III Synthesis and Characterization of α -Fe₂O₃ Nanoflakes and Their Field Emission Properties

Figure 3.10 (a) Typical field-emission current density – applied field (J - E) curves of the α -Fe₂O₃ nanoflake films before and after 100 W Ar plasma treatment. Inset shows the F - N plots ($\ln(J/E^2)$) versus $1/E$ accordingly, which exhibits a good linear dependence (solid line is the fitting result). (b) Long-term stability measurement of FE property of nanoflake films after Ar plasma treatment.

3.6 Summary

Single-crystalline α -Fe₂O₃ (Hematite) nanoflakes were successfully synthesized by a simple Heat-Oxide reaction within the temperatures range of 260 – 400 °C. The nanoflakes synthesized at the lowest temperature—260 °C, show an ultra-sharp morphology: 5 – 10 nm in thickness, 1 – 2 μ m in length, 20 nm in base-width and around 5 nm at the tips. The formation and growth of α -Fe₂O₃ nanostructures are discussed based on the surface diffusion mechanism. The large-scaled α -Fe₂O₃ nanoflake film demonstrates promising electron FE properties and represents the potential applications as future FE electron sources and FEDs. With further treatment by Argon plasmas, its influence on the morphology and crystal structures of nanoflakes are systemically investigated. Significant improvement of field-induced electron emission from the plasma-treated nanoflakes is observed. The TEM investigation shows that the plasma treatment effectively removes amorphous layers and creates plenty of sub-tips on the surface of nanoflakes, which are believed to contribute the enhancement of emission. This work suggests that plasma treatment

CHAPTER III Synthesis and Characterization of α -Fe₂O₃ Nanoflakes and Their Field Emission Properties

technique could be a direct means to improve FE properties of nanostructures.

CHAPTER IV Synthesis and Characterization of Single Crystal Potassium Tungsten Bronze Nanostructures

**CHAPTER IV SYNTHESIS AND
CHARACTERIZATION OF SINGLE CRYSTAL
POTASSIUM TUNGSTEN BRONZE
NANOSTRUCTURES****4.1 Introduction**

This chapter introduces the synthesis and characterization of the novel potassium tungsten bronze (PTB) nanostructure films. Field emission (FE) measurement and emission current stability test are performed. The electrical transport property of individual PTB nanowire devices is investigated and the metallic property of the nanowire is studied. Raman image and orientation dependent Raman measurements are also carried on the individual PTB nanowire.

4.2 Morphology and crystal structure

The morphology of the as-prepared samples is examined by scanning electron microscopy (SEM) (JEOL JSM-6700F) for the analysis of topographical morphologies while the compositions of 1D and 2D PTB nanostructures are characterized by X-ray diffraction (XRD) (Bruker D8 with Cu K_α irradiation) and micro-Raman spectroscopy (Witech CRM200, $\lambda_{laser} = 532$ nm). Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) (JEOL JEM 2010F, 200 kV) are used to investigate the crystal structure of the samples while energy dispersive X-ray spectrometry (EDS) incorporated into the TEM chamber is employed to determine the elemental composition of these nanostructures.

After being heated at 450 °C for 10 hours in air, the pre-treated tungsten foil is found to be covered with a layer of randomly oriented nanowires with diameters and lengths

CHAPTER IV Synthesis and Characterization of Single Crystal Potassium Tungsten Bronze Nanostructures

in the range of approximately 50 ~ 200 nm and 5 ~ 10 μm as shown in Fig. 4.1 (a), respectively. The highest aspect ratio of length to diameter is established to be 100 and the average aspect ratio of these nanowires is around 50, which may result in promising FE properties. It is also noted that the morphologies of PTB nanostructures are able to be tuned from nanowires to nanosheets by simply increasing the heating temperature. When the growth temperature rises to 500 $^{\circ}\text{C}$, the morphology of the nanostructures will gradually change from wire to the sheet shape. And then with increasing growth temperature to 600 $^{\circ}\text{C}$, the density of the nanosheets on the substrate and their size will further increase. (Fig. 4.1 (b) and (c)) The detailed growth mechanism of these nanostructures will be introduced in Section 4.3.

Figure 4.1 SEM images of the as-prepared sample with heating temperature of (a) 450 $^{\circ}\text{C}$ (b) 500 $^{\circ}\text{C}$ (c) 600 $^{\circ}\text{C}$ and duration of 10 hours. The inset shows high magnification SEM image of the $\text{K}_{0.33}\text{W}_{0.944}\text{O}_3$ nanostructures.

Fig. 4.2 shows XRD pattern of the as-prepared samples with different morphologies. All the reflection peak of the nanowire film can be indexed to the hexagonal PTB $\text{K}_{0.33}\text{W}_{0.944}\text{O}_3$ (JCPDS file No. 81-0005) and no impurities peak is identified in its XRD pattern. (Fig. 4.2 black line) However, the difference on the aspect ratios of crystal orientations and extra reflection peaks provide further evidence for the multiple growth directions of PTB nanosheets. (Fig. 4.2 red line)

CHAPTER IV Synthesis and Characterization of Single Crystal Potassium Tungsten Bronze Nanostructures

Figure 4.2 XRD pattern of the as-prepared sample: nanowire (black) and nanosheet (red).

The crystal structures of nanowire and nanosheet are studied by HRTEM. The fringe spacing of 0.38 nm (Fig. 4.3 (b)) concurs well with the interplanar spacing of (001) plane of hexagonal $K_{0.33}W_{0.944}O_3$ (JCPDS file No. 81-0005), revealing the single crystalline structure of synthesized PTB nanowires and a growth direction of [0001]. The selected area electron diffraction (SAED) pattern with the zone axis $[0\bar{2}0]$ (inset of Fig. 4.3 (a)) further confirms the single crystalline property of the nanowires. For the nanosheets, one major fringe spacing along the c -axis coincides with the growth direction of the nanowires, and another fringe spacing of 0.27 nm reveals another competitive growth direction of $[11\bar{2}0]$ (Fig. 4.4 (b)).

CHAPTER IV Synthesis and Characterization of Single Crystal Potassium Tungsten Bronze Nanostructures

Figure 4.3 (a) Low magnification TEM image of the $\text{K}_{0.33}\text{W}_{0.944}\text{O}_3$ nanowire. (b) HRTEM image of the nanowires with growth direction $[001]$. (c) The selected area electron diffraction (SAED) pattern (circled region) of nanowires which indicates good agreement with the diffraction pattern of $\text{K}_{0.33}\text{W}_{0.944}\text{O}_3$ from the zone axis of $[0\bar{2}0]$.

Figure 4.4 (a) Low magnification TEM image of the PTB nanosheet. (b) HRTEM image of the PTB nanosheet. The inset is the FFT image of lattice fringes in (b).

Consequently, the maximum ratio of alkali-metal content is around 0.33 assuming the composition ratio of W is set to be 1.²¹ The elemental ratios of potassium to tungsten in nanowires/nanosheets is investigated by recording EDS data during TEM observation. The sample spectrum and atom ratios are shown in Fig. 4.5.

CHAPTER IV Synthesis and Characterization of Single Crystal Potassium Tungsten Bronze Nanostructures

Figure 4.5 (a) EDS data for the hexagonal PTB nanowire. (b) EDS data for the hexagonal PTB nanosheet.

The average ratios of K/W among different nanowires and nanosheets are equal to 0.35 and 0.39, respectively, which is in good agreement with the XRD and TEM results. The chemical composition of the nanowires and nanosheets can be verified to be hexagonal PTB $K_{0.33}W_{0.944}O_3$ from these data. The data deviation may indicate the existence of more W atom vacancies in our PTB nanostructures compared with pure $K_{0.33}W_{0.944}O_3$ material. It is widely accepted that EDS results have errors in the range of about 5% for a homogeneous material, and can be larger for the present mixture materials. The present EDS results are obtained to indicate the approximate chemical composition in concentrate.¹⁸⁶

The micro-Raman spectrum is also employed to characterize the difference on the crystal structure between the nanowire and nanosheet films. In the Raman spectra of both PTB nanostructure films, there are three groups of peaks (Fig. 4.6). The two peaks at 971 and 910 cm^{-1} can probably be attributed to $-W=O$ stretching. The two strong peaks with the frequencies of 723 and 809 cm^{-1} are assigned to $O-W-O$

CHAPTER IV Synthesis and Characterization of Single Crystal Potassium Tungsten Bronze Nanostructures

stretching modes in WO_6 octahedral units, while the two peaks with frequencies of 667 and 600 cm^{-1} also belong to this group. However, these two peaks are not active in the polarization of the nanosheet samples. This behavior is very similar to the results of single-crystal hexatungstates.¹⁸⁷ The other peaks from the frequencies of 480 to 150 cm^{-1} correlate to the O-W-O bending modes.

Figure 4.6 Single-crystal Raman spectra of nanowire (black) and nanosheet (red).

Similar to $\alpha\text{-Fe}_2\text{O}_3$ nanoflakes, we can deduce the growth mechanism of these PTB nanostructures from these characterization results and *in situ* SEM observation of nanostructures during the growth process in next section.

4.3 Growth mechanism of potassium tungsten bronze nanostructures

The synthesis process of potassium doped tungsten oxide nanowire and nanosheet has been introduced in Section 1.2.3. Fresh tungsten foils are directly heated on a hotplate with potassium hydroxide as catalyst and dopant source. The heating temperature varies in between 450 and 600 $^{\circ}\text{C}$ and the duration was fixed at 10 hours. The growth mechanism of 1D nanowire and 2D nanosheet will be discussed below.

CHAPTER IV Synthesis and Characterization of Single Crystal Potassium Tungsten Bronze Nanostructures

4.3.1 Growth mechanism of the PTB nanowire

Vapor-based growth mechanisms have been intensely studied and widely used to explain the growth of tungsten bronze and tungsten oxide nanowires.^{66, 70} In previous works,^{66, 70} vapor-liquid-solid (VLS) mechanism is constantly employed to describe the growth process of tungsten bronze nanowires. Here, SEM and TEM are adapted to investigate the PTB nanowire growth mechanism directly in this work. With careful observation, not a single-catalyst particle in the nanowire is found in both TEM and SEM images. To elucidate the issue what the growth takes place at the tip or the root of nanowires, dynamic growth process of a specific individual nanowire is monitored by SEM. As shown in Fig. 4.7, further heating only causes an increase in the length on the top (narrow part) while the bottom part remains the same length at low temperature below 500 °C. Therefore, it is found that tip-growth Vapor-Solid (VS) mechanism is the dominant growth mechanism in this work. The continuous growth with the absence of particle at the tip further supports this conclusion. Crystalline (the XRD pattern and Raman spectrum are not shown here) mixture consisting of tungsten-potassium-oxygen (W-K-O) compound such as $K_{0.33}WO_3 \cdot 22H_2O$, which may be resulted from the reaction between W and KOH solution is observed on the W foil which is sonicated in KOH solution and dries in air. Upon heating, tungsten bronze hydrate releases water molecules in its crystalline framework and initiates the evaporation. Once the vapor reaches super-saturation level, nucleation of $K_{0.33}W_{0.944}O_3$ at the top layer of substrate occurred. The continuous nucleation along an energetically favorable direction such as [0001] causes the growth of short nanorods. The subsequent growth of nanowires then results from accumulation of the molecules at the tip of nanorods until the source is used up or the heating process stops. Another possible channel which might contribute to the tungsten bronze vapor is the reaction between W and KOH as proposed in ref.¹⁸⁷

CHAPTER IV Synthesis and Characterization of Single Crystal Potassium Tungsten Bronze Nanostructures

Figure 4.7 (a) SEM image of the as-prepared sample with heating temperature of 450 °C and duration of 1 hour. (b) SEM image of the same nanowires in (a) after being heated for an additional 1 hour at 450 °C.

4.3.2 Growth mechanism of the PTB nanosheet

The growth process of the 2D PTB nanostructures is based on but different from that of 1D ones. The most obvious distinction is that the crystal growing of sheet-like 2D structures is along many directions simultaneously. The TEM and SEM are also employed to investigate the growth mechanism of these nanosheets. The energetically favored crystal growth direction is along the *c*-axis orientation [0001] at temperatures below 500 °C due to the growth mechanism of PTB nanowires. However, as heating provides high concentration of tungsten bronze vapor and much growth energy, higher heating temperatures will enhance the possibility of growth along other crystal directions, as such the growth direction of PTB nanostructures will not be limited to being along [0001] above 500 °C. There will be a joint effect among the driving forces of different growth directions which leads to the formation of different morphologies, *i.e.* nanosheets and nanobelts, at different reaction temperatures, which

CHAPTER IV Synthesis and Characterization of Single Crystal Potassium Tungsten Bronze Nanostructures

are shown in Fig. 4.8.

Figure 4.8 (a) SEM image of the as-prepared sample with heating temperature of 550 °C and duration of 1 hour. (b) SEM image of the same nanowires in (a) after being heated for an additional 1 hour at 550°C.

The detailed growth mechanisms of PTB nanosheets are described as follow: Upon the temperature increasing from room temperature, the same process is identical to the original part of the PTB nanowire growth. Once the PTB vapors have reached saturation level, the vapors condense and then nucleate onto the whole substrate surface in the form of PTB nanoclusters. The growth energy along the [0001] direction is much lower than other directions, so the vapor molecules prefer this direction for further adsorption. After that, with increasing temperature and enlargement of growth energy, the vapor source not only accumulates along the [0001] direction but also deposits on the $[11\bar{2}0]$ one (Fig. 4.4) until the source is used up or the heating process stopped.

It is summarized that the morphology and density of PTB nanostructures can be controlled by varying the heating temperature. The sheet-like PTB nanostructures can not contribute to electron emission due to their small aspect ratios, and the FE properties of PTB nanowire will be discussed in Section 4.5. In the following part, we

CHAPTER IV Synthesis and Characterization of Single Crystal Potassium Tungsten Bronze Nanostructures

will focus on the electrical and optical properties on the individual PTB nanowires.

4.4 Electrical transport in individual nanowire device

Until now the electrical transport properties of PTB nanowire have not been systemically studied yet. The fabrication and electrical measurement configuration of individual nanowire back-gate field effect transistor (FET) is described in Section 2.2. The electrical measurement is performed in air at room temperature. Fig. 4.9 (a) shows the $I_{ds} - V_g$ (source-drain current vs. gate voltage) curve of this FET. It is clearly seen that I_{ds} is hardly affected by the gate potential changes and the resistance of the device is rather low, demonstrating the good conductive and possible metallic property of this PTB nanowire devices.

Figure 4.9 (a) $I_{ds} - V_g$ curves of the single PTB nanowire transistor as a function of gate voltage V_g at source-drain voltage $V_{ds} = 3$ V. (b) Plots of source-drain current I_{ds} vs. voltage V_{ds} at different gate voltage V_g .

For further understanding on its electrical properties, the studies on resistivity are carried out on the same device. The linear $I_{ds} - V_{ds}$ curves at different gate voltage indicate that the characteristics of our device fit Ohm's law well. (Fig. 4.9 (b)) From Ohm's law, the resistivity of the nanowire can be calculated as $\rho = (RA)/L$ (ρ is resistivity, R is resistance, A is cross-sectional area, L is effective length). The measured resistance includes the metal–nanowire contact resistance and the resistance

CHAPTER IV Synthesis and Characterization of Single Crystal Potassium Tungsten Bronze Nanostructures

of the nanowire itself. The diameter of the nanowires varies from 50 to 100 nm, which determines their cross-sectional areas at between $7.85 \times 10^{-15} \text{ m}^2$ and $3.14 \times 10^{-14} \text{ m}^2$. So the calculated resistivity of this nanodevices is around 2×10^{-4} to $8 \times 10^{-4} \Omega \cdot \text{cm}$, which is orders of magnitude lower than that of crystallized tungsten oxide thin films.¹⁸⁸ In general, electrical transport property is governed by doping profile as observed in semiconductor materials¹⁸⁹ and is limited by the oxygen vacancies where the electrons are the major carriers.¹⁹⁰ In our case, nearly perfect crystalline structure which is confirmed by Raman imaging discuss in next section and the low resistivity lead to better electrical transport performance rather than those of heavily n-doped Si materials ($\approx 10^{20} \text{ cm}^{-3}$).¹⁹¹ In addition, the electrical transport properties of nanostructures may be employed to represent the electronic structures of materials themselves. Especially, the surface electronic structure of nanostructure emitter plays a critical role in its FE process. Usually, the method adopted to modify the surface electronic structure of material is altering its Fermi level (work function). In the FE measurement of PTB nanowire, it is very difficult to modify its work function, however, the Fermi levels of different crystal surfaces in PTB materials are different due to their anisotropic crystal structure.¹⁹² It is proposed that the work function (which is defined by the energy difference between Fermi energy level and vacuum level) along the PTB nanowire growth direction is lowest among all crystal directions. Moreover, the anisotropic crystal structure of PTB nanowire has anisotropic resistivity.¹⁹³ The electrical resistivity in the plane perpendicular to *c*-axis (growth direction of nanowire) is much lower than the one along the *c*-axis. These anisotropic properties make electron tunneling easily from the tip of PTB nanowires. Some further experimental and theoretical simulations can be expected.

4.5 Polarized micro-Raman scattering of individual nanowire

Raman scattering is a well-established technique for elucidating structural properties of nanostructures. Micro-Raman studies on individual nanowires such as

CHAPTER IV Synthesis and Characterization of Single Crystal Potassium Tungsten Bronze Nanostructures

SiC,¹⁹⁴ ZnSe¹⁹⁵ and CuO¹⁶ have demonstrated its impressive potential for probing crystal properties of the basic building block in nanoscience and nanotechnology. Usually the width of 1D nanostructured materials is smaller than the wavelength of the excitation laser, so the anisotropic geometry of the sample becomes a contributing factor to the Raman spectra because the effective electric field inside the sample can be distinct on the polarization for samples with a large geometry aspect ratio, which is normally known as the depolarization effect. However, to the best of our knowledge, there is no polarized micro-Raman scattering study report on individual PTB nanowires.

Fig. 4.10 (a) shows the schematic diagram of the setup for polarized micro-Raman scattering investigation on an individual $K_{0.33}W_{0.944}O_3$ nanowire (optical image shown in Fig. 4.10 (b)). The x-axis is set to be coincident with the c-axis of the hexagonal structure which is also the long-axis of the nanowires. By rotating the half-wave plate, the polarization of the incident laser beam is able to be tuned with respect to the long-axis of the nanowires. The polarized Raman signals are distinguished by a polarizer. As shown in Fig. 4.10 (c), there are three groups of Raman peaks in the regions of 900 – 980, 600 – 850 and 200 – 400 cm^{-1} , which could be assigned to W = O stretching, O – W – O stretching and O – W – O bending modes, respectively.¹⁸⁷ The appearance of the two Raman bands in the 900 – 980 cm^{-1} region may indicate the presence of terminal W = O bonds which may support our previous speculation that the nanowires contain W atom vacancies.¹⁸⁷ According to the relationship between the wave number (ν) of a Raman-active W = O stretching mode with bond length (d): $\nu = 25823 \exp(-1.902d)$,¹⁹⁶ the lengths of the corresponding W = O bonds were estimated to be 1.728 and 1.764 Å. Moreover, it is worth to note the bandwidth of the Raman mode of around 960 cm^{-1} is quite small ($\sim 7 \text{ cm}^{-1}$) which may suggest that the W vacancies are arranged in order. The polarization measurements (Fig. 4.10 (c)) clearly show that both the O – W – O and the W = O stretching modes are sensitive to the polarization of the incident laser beam. When the E -field of laser is parallel to the nanowire, the O – W – O stretching bands are much stronger than the W = O stretching bands while the latter significantly increase and become comparable with the former

CHAPTER IV Synthesis and Characterization of Single Crystal Potassium Tungsten Bronze Nanostructures

when there is a 90 degree angle between the polarization of the laser and the nanowire. The intensity of W = O stretching bands is around 5 times more intense in the $Z(YY)\bar{Z}$ polarization than that in the $Z(XX)\bar{Z}$ polarization. The apparent polarization dependence of Raman modes observed here is very similar as that of the single crystal hexatungstates¹⁸⁷ and effectively demonstrates the monocrystalline structure of our PTB nanowires. To further determine whether the whole nanowires are single crystalline or not, polarized Raman mapping is performed. Fig. 4.10 (d) and (e) show the polarized Raman mapping images of the individual nanowire with different polarization geometries as illustrated. These Raman images are plotted based on the ratio of the intensity of the W = O stretching bands over the O – W – O stretching bands. Besides the different contrast due to different polarization dependences, both images appear as a uniform contrast distribution along the entire nanowire. The absence of any local polycrystalline domain which exhibits unpolarized dependence readily shows that the nanowire is one piece of single crystal of high quality.

CHAPTER IV Synthesis and Characterization of Single Crystal Potassium Tungsten Bronze Nanostructures

Figure 4.10 (a) Schematic diagram of setup for the polarized Raman scattering characterization, (b) Optical image of individual $\text{K}_{0.33}\text{W}_{0.944}\text{O}_3$ nanowire, (c) polarized Raman spectra of the nanowire shown in (b), (All peaks were normalized to the strongest peak locating at 790 cm^{-1}) (d) and (e) Raman mapping images of the nanowire shown in (b) by plotting the intensity ratio between the $\text{W} = \text{O}$ stretching bands to the $\text{O} - \text{W} - \text{O}$ stretching bands with different polarization geometries as illustrated.

With the help of HRTEM observation and polarized Raman image, it is shown that there is no layer by layer interface and no local polycrystalline domain in the crystalline PTB nanowire. This result will benefit the electrical transport properties

CHAPTER IV Synthesis and Characterization of Single Crystal Potassium Tungsten Bronze Nanostructures

due to the absence of the electron scattering at the crystal domain boundaries and interfaces, which will further facilitate the electron emission process of these nanowires.

4.6 Field emission from nanowire films

Fig. 4.11 (a) gives the typical current density – electric voltage (J – V) curve of the $K_{0.33}W_{0.944}O_3$ nanowire films. It shows a low turn on field (E_{to}) of 7 V/ μ m and a large current density of 1.4 mA/cm² at a field of 11 V/ μ m. In this measurement, E_{to} is defined by the emission current achieving 10 μ A/cm². The exponential dependence between the emission current and the applied field, plotted by the $\ln(J/E^2) \sim 1/E$ relationship (inset of Fig. 4.11 (a)), indicates that the FE behavior of $K_{0.33}W_{0.944}O_3$ nanowire films follows the Fowler–Nordheim (F – N) relationship.¹²³ The experimental data can be fitted by the simplified F – N equation (1.5) which has been mentioned in Section 1.3.3. The dots are the emission current data the red solid line is the corresponding fitted curve. (Fig. 3.6) For $K_{0.33}W_{0.944}O_3$, the work function ϕ is assumed to be 1.76 eV.¹⁶⁶ Here, due to the large aspect ratio of nanowires, E is usually much stronger than the “applied field”, E_{appl} . β is the field enhancement factor depending on the aspect ratio of the nanostructures, crystal structures and the density of the emitting points, which is defined by the equation (1.6) described in Section 1.3.3. The average spacing between the electrodes d is fixed at 100 μ m in this work. β is obtained to be 221 from the linear fitting of the F – N curve at turn-on area and the maximum emission current density of 1.4 mA/cm² is obtained under a voltage of 1.1 kV. Compared with pure $W_{18}O_{49}$ nanowire⁵⁵ and WO_3 nanotips¹⁴⁵ which were synthesized by typical CVD process, the turn on field of our K-doped WO_3 is much lower and the enhancement factor is much higher regardless the difference of experimental setups. This result shows that the doped K^+ ions can effectively improve the electron transport property in the potassium tungsten bronze, lower the band gap between substrate and nanostructures, and enhance its FE properties furthermore. The FE stability of PTB nanowire film

CHAPTER IV Synthesis and Characterization of Single Crystal Potassium Tungsten Bronze Nanostructures

sample is also investigated and the typical results are shown in Fig. 3.16 (b). The total emission current is monitored over time under an applied macroscopic field of $9 \text{ V}/\mu\text{m}$. While the emission current density is steady at around $350 \mu\text{A}/\text{cm}^2$, the fluctuations are less than 10 % and no degradations are observed. The FE properties of PTB nanosheets are also tested, although no significant electron emission is observed. As mentioned before in Section 1.4, there are two factors affecting the FE performance of nanostructure arrays. The screening effect embodies the density of the nanostructures¹⁹⁷ and the geometry effect embodies the structure morphology, especially the length to width aspect ratios of nanostructure. So the PTB nanosheet with high spatial density and low aspect ratios will hardly generate electron emission under the low electric field applied to nanowire samples (Fig. 4.11).

Figure 4.11 Typical field-emission current density–voltage (J – V) curves of $\text{K}_{0.33}\text{W}_{0.944}\text{O}_3$ nanowire films. Inset shows the F – N plots ($\ln(J/E^2)$ versus $1/E$) accordingly, which exhibits a good linear dependence; (b) Long-term stability measurement of FE property of nanowire film samples shown in Fig. 3.6 (a).

4.7 Summary

In conclusion, single-crystalline PTB nanostructures have been synthesized under ambient condition using a Heat-Oxide method at variable temperatures from 450°C to 600°C . The VS growth mechanism is proposed to explain the growth of these

CHAPTER IV Synthesis and Characterization of Single Crystal Potassium Tungsten Bronze Nanostructures

nanostructures. The tip growth process of nanowire is observed by SEM and TEM. The electrical transport properties show that $K_{0.33}W_{0.944}O_3$ nanowires possess very low resistivity, which indicates that they could be an outstanding contact material for nano-electronic devices. The single crystallinity of nanowires has also been demonstrated by polarized Raman mapping on individual nanowires. Furthermore, FE investigations demonstrate the promising emission properties of $K_{0.33}W_{0.944}O_3$ nanowire films. With further improvements, PTB nanowires could become one of the potential candidates for future FE electron sources and FEDs.

CHAPTER V Field Emission Properties of Individual Potassium Tungsten Bronze Nanowire

CHAPTER V FIELD EMISSION PROPERTIES OF INDIVIDUAL POTASSIUM TUNGSTEN BRONZE NANOWIRE

5.1 Introduction

In this chapter, field emission (FE) of individual potassium tungsten bronze (PTB) nanowire is studied. The experimental data indicate that the FE results agree with the Fowler-Nordheim ($F-N$) theory very well. The relationship of field enhancement factor (β) with the shape of counter anode, the inter-electrode distance and the angle between two electrodes are systemically investigated. In addition to the typical anode-cathode setup, a third probe is introduced and functioned as one single-sided gate. The measurement results of this triode type FE device indicate that the side-gate voltage could significantly affect the turn on electric field E_{to} and enhancement factor β . The finite element simulation results are consistent with the experimental results.

Six individual PTB nanowire emitters are shown in Fig. 5.1 and only one typical set of FE measurement results including its FE evaluating indicators is selected to be discussed later on.

CHAPTER V Field Emission Properties of Individual Potassium Tungsten Bronze Nanowire

Figure 5.1 SEM images of the individual PTB nanowires attached to the electrochemically etched tungsten tip.

5.2 Anode shape influence

The FE properties of the individual nanostructure are not only dependent on the properties of the material and the geometry of cathodes but also related to the material and geometrical properties of the anode.¹¹⁴ In this thesis, the anode geometry dependence on the FE process of individual PTB nanowire are studied systematically with a typical two-electrode configuration.

5.2.1 Experimental results and discussion

The FE measurements are performed as a function of the inter-electrode distance. The inter-electrode distance d can be adjusted from several to tens of micrometers. (Fig. 2.7 (a) and (b)) For flat plane anode, the diameter of nanowire is 104 nm and length is around 7.2 μm ; for needle tip anode, the diameter is 86 nm and length is around 7.6 μm . (Fig. 5.2 (a) and (b))

CHAPTER V Field Emission Properties of Individual Potassium Tungsten Bronze Nanowire

Figure 5.2 The SEM images of FE measurements as different anode types. (a) Flat plane anode: the diameter of the nanowire is 104 nm and length is around 7.2 μm . (b) Needle tip anode: the diameter of the nanowire is 86 nm and length is around 7.6 μm .

The corresponding I - V curves in case of the flat plane and the needle tip anode are plotted in Fig. 5.3 (a) and (b), respectively. The compliance current is set to below 100 nA in order to avoid device failure, possibly due to Joule heating on the junction between the nanowire and the tungsten tip.¹⁶³ It can be observed that E_{to} which is defined as the applied field required for I_{eds} of 20 nA, decreases when the anode is moved away for both anode types. For tip anode with inter-electrode distance of 6 μm , the E_{to} is 37 V/ μm , which is larger than the value of 12.7 V/ μm for flat plane anode. As the distance is increased to 10 μm , the E_{to} reduces to 25 V/ μm . Subsequent increase of the distance to 15, 20, 30 and 40 μm results in E_{to} of 18.1, 15.6, 11.6 and 8.8 V/ μm , correspondingly as seen in Fig. 5.3 (a). Fifty micrometers is the largest distance due to the limit of measurement accuracy as beyond this range the nanowire can not be resolved clearly at such a magnification.

The individual nanowire FE behavior follows the F - N theory as^{198, 199}

CHAPTER V Field Emission Properties of Individual Potassium Tungsten Bronze Nanowire

$$I = A \times J = A \times \frac{k_1 \beta^2}{\phi} \left(\frac{V^2}{\beta^2} \right) \exp\left(\frac{10.4}{\sqrt{\phi}}\right) \exp\left(-k_2 \frac{\phi^{\frac{3}{2}} d}{\beta V}\right) \quad (5.1)$$

where I is the emission current (ampere), V is the applied voltage (volt), ϕ is the work function of the emitter, A is the emission area (m^2), β is the effective-field enhancement factor, $k_1 = 1.56 \times 10^{-6} \text{ AV}^{-2} \text{ eV}$, $k_2 = 6.83 \times 10^9 \text{ V eV}^{-3/2} \text{ m}^{-1}$.

Herein, the F - N curves for both anode types can be fitted to straight lines, as shown by the curve fit in Fig. 5.3 (c) and (d) (red line), indicating that the FE process of individual nanowire satisfies the F - N law quite well.²⁰⁰ The field enhancement factor, β , which is important to determine the FE properties of nanowire,^{201, 202} can be extracted from the slope (S) of the F - N curve [$\ln(I/V^2)$ vs. $1/V$] using the equation:

$$S = -k_2 \phi^{\frac{3}{2}} \frac{d}{\beta} \quad (5.2)$$

According to equation (5.2), if the work function is known, the field enhancement factor β can be deduced. Herein, the relationships between β and d obtained for the different morphology anodes are shown in Fig. 5.4 (a).

This relationship is dependent on many influencing factors such as the complication of the measurement environments and the sample condition. So many models have been proposed to explain it in previous studies.^{158, 203, 204} According to the previous experimental and simulated results, there are three FE models on individual emitters as follow:

1) The tip-tip model^{158, 164, 204} which the enhancement factor β will increase to an asymptotic value as d increases. This model can be described as the Edgcombe and Valdre function^{158, 205}:

$$\beta = \beta_0 + \left(1 + A \times \frac{d+l}{d} - B \times \frac{d}{d+l}\right) \quad (5.3)$$

CHAPTER V Field Emission Properties of Individual Potassium Tungsten Bronze Nanowire

where l is the length of the nanowire, A and B are constants.

2) The plane–plane model²⁰³ which the enhancement factor β approaches a value depicted by l and r alone and is described by the expression $\beta = (1 + \sqrt{\frac{l}{\alpha r}})^m$ where l

is the length of the nanowire, r is the radius of the nanowire tip curvature, the $\alpha = 2$ and $m = 1$. The value of α and m is fitted from simulation results.

3) The tip-plane model^{114, 141} which the anode can be thought of as a plane electrode, and the cathode as a long needle. In this model, the description of the relationship between the β and the d is linear.

With the help of these three models, the FE process of an individual PTB nanowire is similar to that of a carbon nanotube¹¹⁴ and accords with the tip–plane model.

From the large area measurement mentioned in Section 4.6, we obtained a field enhancement factor β of 221 over an area of 0.28 cm^2 at $d = 100 \text{ }\mu\text{m}$, and the voltage needed to extract 1 nA per emitter ($10 \text{ }\mu\text{A}/\text{cm}^2$) is 700 V.²⁰⁶ From the individual nanowire FE measurement, the onset voltage needed to extract 1 nA current is lower, but the value of β is a bit smaller than that of a mass of wires. It might be because the distance d ($\leq 50 \text{ }\mu\text{m}$) in this measurement is smaller than that in large scale sample. In accordance with the trend of β vs. d , the β value of individual nanowire would be much larger than that of film samples at the same d due to the elimination of the electron screening/shielding effect.

CHAPTER V Field Emission Properties of Individual Potassium Tungsten Bronze Nanowire

Figure 5.3 The current–voltage (I – V) curves of individual PTB nanowire with flat plane anode setup (a) and needle tip anode setup (b). (c) and (d) The corresponding F – N plots ($\ln(I/V^2)$ versus $1/V$) accordingly, which also exhibits a good linear dependence.

5.2.2 Simulation results and analysis

The use of electrostatic field simulations continues to be an important and valuable tool in the electronics researches. In this thesis, the electric field distribution near an isolated nanowire in the FE process is simulated by using finite element method as well. Here the commercial computer software COMOSOL MULTIPHYSICS © 3.3 is selected to carry out the simulation by solving the Laplace's equation in two dimensions. And the electrostatic magnetic mode is chosen to simplify the simulation setup and process. Accurate simulations of electrostatic field can be performed on a wide range of experimental setups, such as different morphological types of anode

CHAPTER V Field Emission Properties of Individual Potassium Tungsten Bronze Nanowire

and different inter-electrode distances. Due to the simulation condition setup, the work area or width is kept larger than 200 nm² which is enough to ensure no field screening due to edge effects. Also the environment boundary is set to insulator and its potential is equal to 0 V. The isolated emitter is set as a rectangle with the width of 100 nm and the length of 10 μm, which is considered as a 2D cross-section projection of nanowires. A mesh or grid is automatically determined by the software over the whole simulation area, however, the density of intersection points are then manually increased to around the emitter tip to allow the local electric field E could be accurately extracted. Exactly, a mesh line spacing of 0.5 nm is used at and around the tip.

The tungsten tip in experimental cathode part is not included in the simulation setup in order to simplify the simulation process. In this simulation, the electric potential at the cathode is set to be -160 V for the β vs. d . The counter anode is set to be 0 V. The whole region boundary is set to be electrically insulating. The effective electric field strength E_{eff} is defined as the field at the apex of the emitting tip which can be collected from simulation results. The mean electrical field strength E_{mean} is defined as the average electric field between the two electrodes which is equal to the applied voltage divided by inter-electrodes distance. The theoretical field enhancement factor β_{the} is defined as:

$$\beta_{the} = E_{eff} / E_{mean} \quad (1.12)$$

The simulated results of relationship between β_{the} and d for both types of anodes are shown in Fig. 5.4 (b). The values of β_{the} are extracted when the d value varies from 1.5 to 48 μm. Apart from the value difference of the enhancement factors, it can be clearly observed that the relationship between β_{the} and d of the finite element simulation results (Fig. 5.4 (b)) is similar to the experimental results (Fig. 5.4 (a)). It is indicated that the finite element method can effectively simulate the real electrical distribution in our experiments and have immense potential to be applied in future FE

CHAPTER V Field Emission Properties of Individual Potassium Tungsten
Bronze Nanowire

device design.

Figure 5.4 The relationship between β and the inter-electrode distance d with flat plane anode setup (black) and the tip anode setup (red), shows increasing enhancement with increasing distance. (a) The experimental results. (b) The finite element simulation results.

5.3 Electrodes off-axis influence

The influence of electrodes off-axis on the FE properties has been studied. There are two types of electrodes off-axis. First type is defined as the shift of angle α between the emitter normal direction and a line connecting the two electrodes. As the experiments are conducted in SEM chamber, the angles between two electrodes could be measured accurately. The inter-electrode distance d along the nanowire is kept as a constant of 10 μm and the angle α varies from 0 to 75 degrees. (Fig. 5.5) Second type is defined as the rotation of anode when the inter-electrodes distance is fixed to a constant of 10 μm and the rotation angle γ varies from 0 to 90 degrees. (Fig. 5.7) Here we only employ the electrostatic simulation to verify its influence on the enhancement factor.

CHAPTER V Field Emission Properties of Individual Potassium Tungsten Bronze Nanowire

Figure 5.5 The SEM images of FE measurements under different dislocation angles between the nanowire cathode and the needle tip anode.

In first electrodes off-axis type, it is found that β increases from 0 to 30 degrees, and then decreases from 30 to 75 degrees (Fig. 5.6 (a) black square). This indicates that from 0 to 30 degrees, β is mainly dependent on the geometrical properties of the nanowire. The strongly local electric field is generated at the sharp tips of the nanowire. This localized field increases with the increase of angle α from 0 to 30 degrees and therefore results in the increase of β . The location of the anode becomes more important than the morphology of the anode when the angle α increases from 30 to 75 degrees. Fig. 5.6 (b) shows the simulated distribution of the electric field between the two electrodes. The simulation results shown in Fig. 5.6 (a) is β_{he} for different dislocation angles when the electrical potential at the cathode is set to be -350 V. It is found that the simulation results agree well with the experimental results.

CHAPTER V Field Emission Properties of Individual Potassium Tungsten Bronze Nanowire

Figure 5.6 (a) The relationship of experimental and finite element simulated results between β and the angle α . (b) The finite element simulation of the electric field distribution accordingly.

In second electrodes off-axis type, simulation configuration is set as shown in Fig. 5.7. The anode is rotated around the tip of nanowire and the tip to tip distance is fixed. It is found that the enhancement factor β vs. γ fluctuation is much smaller than that of first type, which shows the inter-electrodes distance is the most important impact factor for electric field enhanced at the tip of emitter. (Fig. 5.8) Also the trend change of the relationship of β vs. γ is different from the first type. The maximum enhancement is present in the $\gamma = 0$ degree, which shows the dominant properties of vertical direction emission current in FE process. All these results suggest that besides of the shape of the electrode, the electrodes off-axis is another important factor for FE behavior of individual emitter.

CHAPTER V Field Emission Properties of Individual Potassium Tungsten Bronze Nanowire

Figure 5.7 The simulation configuration of off-axis angle γ vs. enhancement factor β

Figure 5.8 (a) The relationship of finite element simulated results between β and the angle γ . (b) The finite element simulation of the electric field distribution accordingly.

5.4 Side gate effect

In this section, FE measurements on individual PTB nanowire with the assistance of gate potential were performed and more efficient controllability is expected from

CHAPTER V Field Emission Properties of Individual Potassium Tungsten Bronze Nanowire

the experiments. The experiment setup is introduced in Section 2.4.2. The inter-electrode distance d is fixed at 12.5 μm , the length of the nanowire l is 7.5 μm , the distance between the gate electrode and the emitter d' is 5 μm , and the diameter of the nanowire w is 200 nm (inset of Fig. 2.7 (b)).

5.4.1 Experimental results and discussion

The reproducibility of the gate-controlled individual PTB nanowire FE performance is verified by repeating the measurement on a number of samples. One typical result set of side gate-controlled I_{esd} - V_{esd} curves is plotted in Fig. 5.9 (a). It is found that the turn-on electric voltage (defined as the voltage under which I_{esd} is 50 nA) decreases from 440 V to 267 V while the gate voltages (V_{eg}) increases from 0 V to 100 V. The results indicated that the turn-on electrical voltage can be effectively tuned by controlling the gate voltage. (Fig. 5.9 (a) and table 5.1) And the gate potential will affect the emission electric field which will describe in simulation part.

CHAPTER V Field Emission Properties of Individual Potassium Tungsten Bronze Nanowire

Figure 5.9 Emission properties of the triode type FE setup. (a) Relation of the current I_{esd} vs. applied voltage (V_{esd}) at various V_{eg} as indicated and (b) $F-N$ plot for various V_{eg} as indicated. (c) Plots of FE current I_{esd} and the gate leakage current I_{eg} as a function of side-gate voltage V_{eg} at applied voltage $V_{esd} = 400V$ in the FE experiment. (d) Curve of the transconductance g_m of the FE setup as a function of side-gate voltage V_{eg} .

As reported in literature, it is found that our field emission current-voltage ($I_{esd}-V_{esd}$) characteristics are governed by the space-charge-limited (SCL) flow of current at low biases²⁰⁷ while the $F-N$ model fits the $I_{esd}-V_{esd}$ curves in high voltage regime. (Fig. 5.9 (a)) The $F-N$ plots in Fig. 5.9 (b) also show the non-linear properties which agrees with above results. There are two distinct linear regimes for $F-N$ plots, which is more obvious for high gate voltage in the gate-controlled FE process. These results elucidate the transition from SCL law to $F-N$ law with the increase of gate voltage.²⁰⁸ The transition is also observed in the other two samples we examined. The β value in the $F-N$ regime increases from 74 to 264 while the V_{eg} varies from 0 to 100 V. The linear property of $F-N$ plots shows the gate electric field will not affect the electron

CHAPTER V Field Emission Properties of Individual Potassium Tungsten Bronze Nanowire

emission directly but can be employed to tune the E_{local} near the emitter tips. The value of V_{to} and β obtained from the $F-N$ plot and the equation (5.2) are summarized in table 5.1.

Table 5.1 Relationship between gate voltage (V_{eg}), turn-on voltage (V_{to}) and effective field enhancement factor (β) of the gate-controlled individual PTB nanowire field emission devices.

V_g (V)	0	20	40	60	80	100
V_{to} (V)	440	425	351	296	290	267
β	74	73	82	83	175	264

The side gate potential plays an important role in terminal control, where the gate voltage V_{eg} introduces an extra electrical field to enhance electron emission from PTB nanowire. The gate controllable mechanism in this FE experiment is different from the traditional FET devices, in which the former controls the electric field near the emitter tip and the latter controlled the concentration of the carrier by the gate potential. As shown in Fig. 5.9 (c), for the source-drain electrical voltage $V_{esd} = 400$ V, the I_{esd} vs. V_{eg} curve presents three regimes of interest. The first regime, V_{eg} varying from 0 to 30 V, is called the gate leakage regime where I_{esd} remains steady with an increase of V_{eg} because the emission current can be trapped by the side gate, results from space-charge-limited current flow.¹⁸⁹ The second regime of V_{eg} varying from 30 V to 48 V is called the FE excited regime, where the I_{esd} increases rapidly. At this regime, V_{eg} tends to lower the surface potential barrier with the help of extra electric field and results in the tunneling of great number of electrons from the tip of PTB nanowire to anode. In particular, the side gate structure in our experiment may induce an asymmetric electric field near the surface of the emitter tip which can more effectively enhance the gate electrical field. It has been confirmed by the simulation results. Finally, the saturation regime is reached when V_{eg} is higher than 48 V where the turn-on current is $\sim 3.5 \times 10^{-7}$ A. Due to the metallic properties of PTB nanowires mentioned in Section 4.4, this current saturation regime in Fig. 5.9 (c) may be limited

CHAPTER V Field Emission Properties of Individual Potassium Tungsten Bronze Nanowire

by the carrier (free electron or hole) density rather than doping profile as observed in the semiconductor materials such as ZnO.¹⁸⁹

In the gate-controllable FE process, we also observed that the larger the transconductance g_m , the stronger V_g can influence the FE current. To study the g_m in our FE process, the relation of emission current I_{esd} as a function of gate voltage V_{eg} is presented in Fig. 5.9 (d). The g_m is expressed as:

$$g_m = \frac{dI_{esd}}{dV_g} \quad (5.4)$$

In our study, with a gate voltage of 45 V, the individual PTB nanowire side gate type FE device exhibits a high g_m of 7.7 nS. This value is comparable to other single nanowire FET.²⁰⁹ The curve has a maximum value, indicating there is an optimized low V_{eg} value for controllable I_{esd} . This result shows the good controllability of our experimental configuration which can be widely used in fabricating high vacuum single nanowire FE devices.

5.4.2 Simulation results and analysis

In order to further understand the FE mechanism of individual nanowires with extra gate electrical field, the electrostatic potential distribution is simulated as the function of the variable cathode-anode voltages and gate voltages by a finite element method in 2D mode. Here, the double-side gate setup is adapted to compare with our experimental single-side gate setup and the 2D projection of the real emitter and gate electrode are set as boundary conditions of simulation. Because the double-side gate will produce a symmetrical gate electric field which is simpler and similar to the real FE device setup.²¹⁰ The electric field distribution profiles of double-side gate individual PTB nanowire field emitter and single-side gate one are plotted in Fig. 5.10 (a) and (b), respectively. The double-side gate electrode will provide a symmetric

CHAPTER V Field Emission Properties of Individual Potassium Tungsten Bronze Nanowire

electric field similar to that from the FE device with the gate layer surrounding the emitter.²¹¹ These finite element simulations were employing COMOSOL MULTIPHYSICS © 3.3 to solve the 2D Laplace’s equation²¹² as the simulation method.

Here, due to the large length-to-diameter aspect ratio (≥ 50) of nanowires, the local electric field, E_{local} , is usually much stronger than the “applied field”, E_{appl} , with the field enhancement factor β defined by:

$$E_{local} = \beta E_{mean} = \beta \frac{V}{d} \tag{1.12}$$

where V is the electrical potential and d is the distance between two electrodes.

Figure 5.10 Simulated electric field distribution plot in the PTB nanowire emitter cap under constant anode voltage 400 V. (a) Double-side gate-control. (b) Single-side gate-control. The white and blue colors represent the lower potential area. We can see that large local field exists at the tip of the emitter.

CHAPTER V Field Emission Properties of Individual Potassium Tungsten Bronze Nanowire

Based on the electrical field simulation results shown in Fig. 5.10, it is noticed that the equi-potential surfaces with largest field strength values are closest directly above two tip apices of PTB nanowire 2D projection, indicating that the edges of PTB nanowire may be the position where electrons are most likely to tunnel out of. It might be because of the largest curvatures near the tip edge apices of nanowire. From the color spectrum with the same scale bar of the electric field distribution under the same applied electric field, it is obvious that the electric field (around 1.8×10^9 V/m) near the tip of the single-side gate mode (inset of Fig. 5.10 (b)) is much stronger than that (around 1.0×10^9 V/m) of the double-side gate mode (inset of Fig. 5.10 (a)). The field enhancement factor β also shows the interesting trend proven by the experiment results (Fig. 5.11). (The values of β in simulation work may not be equal to the realistic values) The extracted results show that the β value of single-side gate setup is larger than it of the double-side gate type. It is indicated that the single-side one could be more effectively controllable than the double-side setup for the FE process under same electrical conditions and inter-electrode distance.

Figure 5.11 Calculated results of field enhancement factor (β) for the double-side-gate setup (■) and the single-side-gate setup (●) with different gate voltage.

CHAPTER V Field Emission Properties of Individual Potassium Tungsten Bronze Nanowire

5.5 Summary

In summary, field electron emission properties of individual $K_{0.33}W_{0.944}O_3$ nanowire have been studied. These FE phenomena follow $F-N$ law. The experimental and simulated results indicate that the geometry effect of the two electrodes plays an important role in the FE process of individual PTB nanowire. Furthermore, it is found the extra gate voltage can effectively lower the turn-on voltages while increase the field enhancement factors. The subsequent simulations reveal that the local gate electric voltage induces an extra asymmetric electrical field that is able to enhance electron emission. The transconductance of the gate controllable FE process is about 7.7 nS. This value shows the good controllability of the emission process by the gate voltage. These FE measurements of individual nanowire are also used to explain the large scale sample FE results, which should be of concern future fundamental and especially practical commercial application studies.

CHAPTER VI Conclusion

CHAPTER VI CONCLUSION

In this thesis, a simple, low cost and morphology controllable method has been applied to produce large-scale functional metal oxide nanostructures. Further development will be achieved to control the morphologies of α -Fe₂O₃ and potassium tungsten bronze (PTB) nanostructures by changing the growth parameters such as the growth temperature and the heating duration. Here, I briefly summarize the results and research contributions of this project.

The single crystalline α -Fe₂O₃ nanoflakes have been synthesized by iron–air reaction at temperature ranged from 260 to 400 °C. Surface diffusion mechanism is proposed to account for the growth of these nanoflakes. Good electron field emission (FE) performance is also provided by these ultra-sharp α -Fe₂O₃ nanoflake films fabricated at the low temperature of 260 °C. Furthermore, the effect of Argon plasma treatment on α -Fe₂O₃ nanoflakes is investigated. The results of TEM reveal that it is effectively cleaned the surface of nanoflakes, created plenty of ultra-tiny sub-tips and consequently enhanced the electron emission by this kind of plasma treatment. With the low turn on electrical field, high current density and acceptable emission stability, it is believed that plasma treated α -Fe₂O₃ nanoflakes could be one of the promising candidates as future FE electron sources and displays.

The single crystalline PTB nanostructures have been synthesized by directly heating tungsten foil at various temperatures from 450 to 600 °C with potassium hydroxide as catalyst and dopant elements under ambient condition. The Vapor-Solid mechanism with tip growth process is proposed. The morphology and crystal structure of these nanostructures are characterized by SEM, TEM, XRD and micro-Raman studies. The electron FE properties of K_{0.33}W_{0.944}O₃ nanowire films are also investigated. These results show PTB nanowire could be another candidate for cold cathode nanodevices.

The field electron emission properties of individual K_{0.33}W_{0.944}O₃ nanowire have been systematically studied by *in situ* FE measurements in SEM. All these FE results

CHAPTER VI Conclusion

follow Fowler-Nordheim (*F-N*) law. It is indicated that the geometry effects of the two electrodes play important roles on the FE process of the individual nanowire. This study is helpful for deeply understanding FE phenomena of individual nanostructures in physical essence. The extra gate electrical potential can not only effectively lower the turn on voltages but also increase the field enhancement factors of the single-side gate-controlled PTB nanowire FE devices. The transconductance of the gate-controlled FE process is about 7.7 nS. This value shows good controllability of the emission current by gate voltages. In the wake of further studies on the applications of PTB nanostructures, it is believed that these nanostructures could be the promising candidates as future microelectronic devices. We hope the current work can contribute to the further researchers on the nanostructure fabrication and its technological applications.

There are still unknown research area needs to be explored in depth for 1D and Q1D metal oxide nanostructures. For instance, it is necessary to understand the profound mechanism and physical properties in order to make any improvements on their practical application level. These α -Fe₂O₃ and PTB nanostructures provide an excellent opportunity for physicists to explore new physics and novel applications on the nature of the materials with open boundaries.

Recommendations for future work are as follows:

1. The effect of geometrical parameters of the individual nanowire FE device on their field enhancement factor β need to be investigated, including the radius of the nanowire emitter, the gate-cathode and gate-anode distance. The theoretical electrostatic calculation should also be performed. All the results of experimental and theoretical calculation can provide useful information in the fabrication and design of the gated individual cold cathode emitter for field emission display panels and other nanoscale triode devices.
2. The micro-fabricated metal oxide nanowire field-emitter arrays with gating control can be employed as a microwave amplifier. It is worth to demonstrate the high frequency AC signal amplifies properties by using our single-side gate adapted of field emission measurement setup.

CHAPTER VI Conclusion

3. Although in this thesis we have systemically studied the relationship of the β and the separation distance of the two electrodes d . The physical law of the β on distance d and the radius of the nanowire r for our tip-plane model setup are still unclear. More effort should be put on the experimental and theoretical aspects.

The research on single carbon atomic layer-graphene is one of the hottest topics in physical and chemical sciences. However, the measurement of FE property for the single layer graphene crystallographically edge with a nanoscale separation gap is still a challenge. Based on our manipulator operating in the SEM chamber, it is convenient to study the FE property and the electrostatic gating effect of the single layer graphene electronic device. Graphene nanogap with atomically edges may open up opportunities for both fundamental and applied research of vacuum nanoelectronics.

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