Fabrication and properties of oxide semiconductor nanowires

Shen, Youde

2016

Shen, Y. (2016). Fabrication and properties of oxide semiconductor nanowires. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/65879>

<https://doi.org/10.32657/10356/65879>

FABRICATION AND PROPERTIES OF OXIDE SEMICONDUCTOR NANOWIRES

Shen Youde

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES
NANYANG TECHNOLOGICAL UNIVERSITY

2015

FABRICATION AND PROPERTIES OF OXIDE SEMICONDUCTOR NANOWIRES

Shen Youde

School of Physical and Mathematical Sciences

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

2015

Citations to Published Work

Majority of Chapter 4 appears as:

“Epitaxy-Enabled Vapor–Liquid–Solid Growth of Tin-Doped Indium Oxide Nanowires with Controlled Orientations” **Youde Shen**, Stuart Turner, Ping Yang, Gustaaf Van Tendeloo, Oleg I. Lebedev, and Tom Wu, *Nano Lett.* **2014**, 14, 4342–4351

Acknowledgements

First and foremost, I would like to thank my supervisors Assoc. Prof. Wu Tao and Assoc. Prof. Wang Qijie for their guidance and support. Prof. Wu recruited me and guided me into the research of nanomaterials. I learned a lot from him and here I want to express my appreciation to him. Prof. Wang was my main supervisor in the last two years during my Ph.D program. Thanks to him for the freedom given to explore and valuable suggestions during my research. Here I am indebted to him.

I would like to thank Dr. Oleg I. Legedev (CNRS, France) and Dr. Stuart Turner (EMAT, Belgium) for the TEM measurement. Thanks to Dr. Yang Ping (NUS) for the RSM measurement. Thanks to Prof. Chen Hongyu (NTU) for the TEM measurement.

I also want to thank Dr. Li Gonping for teaching me how to assemble and use the CVD system. Thanks to the PAP department for allowing me to use the CVD system in the past two years. Thanks to the lab manager Mr. Li Yuanqing for the help in experiments.

I would like to thank all the group members in both Prof. Wu's group and Prof. Wang's group for their help. They are Dr. Ding Junfeng, Dr. Ashok Bera, Dr. Lin Weinan, Dr. Hu Weijin, Mr. James Lourembam, Mr. Gao Jing, Mr. Pu Ling, Mr. Yu Xuechao, Dr. Tao Jin, Dr. Liu Tao, Dr. Liang Guozheng, Dr. Meng Bo, Mr. Hu Xiaonan, Dr. Li Xiaohui, Ms. Yan Zhiyu, Mr. Zeng Yonquan, Mr. Li Benliang, Mr. Song Xiaohui, *et al.* I want to say thanks to them.

I want to express my appreciation to my friends Gong Dangguo and Wang Lei for their friendship and help. They have brought a lot of fun to my life and back up me all the time. Without them, I won't be able to pursue the PhD dream.

I would like to thank NTU Research Scholarship for the financial support.

At last, I want to thank my parents, brothers and sisters, and my girlfriend for their unconditional love and support. They are the most important people to me. Although my parents would never hear my thanks, I want to say "Thank you. I love you and miss you so much".

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Abstract

Semiconductor nanowires have been intensively studied because of their novel properties in the past two decades. Lots of interesting nanostructures have been demonstrated *via* the famous vapor-liquid-solid (VLS) mechanism. This bottom-up synthesis is significant for extensive applications in sensing, photonics, electronics and energy conversion. Studying nanowire growth behaviour and controlling nanowire morphology are the central theme in nanoscience and nanotechnology. Herein, we bring insights to the conventional VLS growth mechanism in the growth of lateral and kinked nanowires and advance the study of Gibbs-Thomson effect in planar nanowires growth.

We report the growth of planar, vertical and randomly oriented tin-doped indium oxide (ITO) nanowires. Those differently oriented nanowires could be grown on yttria-stabilized zirconia (YSZ) substrates with an epitaxial relationship in the VLS mechanism. The growth temperature is the only parameter to be regulated. Our (scanning) transmission electron microscopy and reciprocal space mapping experiments revealed that the substrate-nanowire epitaxy had essential role in the growth of oriented in-plane and out-of-plane nanowires at the higher growth temperatures. On the contrary, the randomly oriented nanowires grew at lower growth temperature. In addition, the control of the symmetry, orientation and structure of the nanowires was also demonstrated by using (110) and (111) YSZ substrates. Based on

these results, we obtained regular arrays of lateral ITO nanowires by using patterned Au catalyst nanoparticles.

Furthermore, we demonstrate the direct observations of the Gibbs-Thomson effect in planar nanowires for the first time. Our systematic studies showed that the growth velocity of planar indium tin oxide (ITO) NWs conformed to Gibbs-Thomson effect and could be modulated by tin doping concentrations in spite of their rich growth directions and complex shapes. A growth model based on the surface energy was developed to explain the increasing cutoff diameter with decreasing tin doping concentration and the different cutoff diameter on different oriented substrates. We demonstrated the unprecedented growth behaviors of indium oxide (IO) nanostructures and revealed the important function of the tin dopants.

At last, we report the growth of kinked single-crystalline In_2O_3 nanostructures consisting of nanocone base and nanowire tip connected without any twin boundaries or stacking faults. During the tailored growth, when the diameter of gold catalyst nanoparticle at the apex of the nanocone shrunk to ~ 100 nm as a result of the gold atom migration, the growth direction switched from $[111]$ to either $[110]$ or $[112]$, depending on the growth conditions. Our results indicated that the size-dependent free energies of different oriented nanowires dictated the switching of growth directions, and the mechanism of forming such novel nanocone-nanowire kinked nanostructure may be universal for a wide range of functional materials.

Chapter 1. Introduction

1.1 Background

In the past half century, since the invention of the PN diode and the transistor in 1940s and 1950s, the semiconductor industry has witnessed a revolution in science and technology and dramatically improved human's life on the planet. The famous Moore's Law, the number of transistors in a dense integrated circuit doubles approximately every two years, is the best footnote of this revolution. From the 1980s, semiconductor manufacturing has entered the era of nanometers scale. Afterwards, the semiconductor manufacturing approached to the sub-100 nm scale around year 2000. The microelectronicmechanical system (MEMS) was replaced by nanoelectronicmechanical system (NEMS). Therefore nanomaterials have become a top popular topic and attracted worldwide scientists' and researchers' interest.

Nanomaterials or nanostructures normally refer to the structures with at least one dimension less than 100 nm. Based on their geometry, nanostructures are usually divided into 0-dimensional nanostructures (quantum dots), 1-dimensional nanostructures (nanowires, nanobelts, nanotubes, *et al.*) and 2-dimensional nanostructures (quantum wells, graphene, MoS₂, *et al.*). The obvious advantages of nanostructures are as follows: (1) Functional unites can be heavily packed because of their tiny size. For example, the transistor density in present Intel CPU is 50 times denser than that 10 year ago. (2) Nanostructure-based devices are portable because the electronic devices built in smaller scales can have the same functions. This advantage makes the wearable electronic devices a reality. (3) Nanostructure-based devices are

less energy and materials consuming. Less energy consuming means the device can work for longer time every single charging. (4) The extremely high surface to volume ratio in the nanostructure makes nanostructure-based devices extremely sensitive and accurate. Today, nanostructure-based devices can even measure the signal of a single DNA molecule/virus.¹ The application of nanostructures in biochemistry is a promising field at high speed.

Moreover, when the materials size is in nanometer scale, usually in the regime of less than 10 nm, materials show new properties induced by quantum effects which cannot be observed in bulk materials. Take the size-dependent band gap of CdSe quantum rods as an example: the band gap of CdSe quantum rods with length of 22 nm and width of 3.6 nm is 2.16 eV; its band gap will shift to 1.93 eV when the length is 40 nm and width is 4.8 nm.² Meanwhile nanomaterials are a good platform for researchers to explore the mystery of nature. The recently emerging research on layered 2D materials like graphene and transitional metal dichalcogenides (TMDs) is an excellent example, which refreshes people's view on materials science. For example, people usually believed that one atomic thin film was not stable because of the thermodynamic instability. But Geim and Novoselov's work changed people's view: graphene have been demonstrated as thinnest, strongest, extremely highly conductive, massless charge carrier, zero-band gap materials.³

The fabrication of nanostructures can be divided into two approaches: top-down and bottom-up. The top-down approach based on the photolithography and chemical etching techniques is a widely-used method. Because of its high throughput and high

quality, the top-down approach has achieved great success in the past several decades and is still under further development. The major drawback of the top-down approach comes from its resolution which is determined by the light diffraction (Rayleigh Criterion). It becomes very challenging to fabricate tiny features when their size enters to sub-100 nm region. In contrast, the bottom-up approach can easily fabricate sub-100 nm nanostructures and even sub-10 nm nanostructures. The bottom-up approach might substitute the top-down approach in the long term. In a bottom-up process, the growth species self-assemble on the substrate surface. Such process allows the bottom-up approach to go beyond the size limits and nanowires are believed to be promising building blocks for the next generation nanodevices.⁴

Within the bottom-up approach, there are three main growth mechanisms: vapor-liquid-solid (VLS), vapor-solid (VS) and vapor-solid-solid (VSS). The key feature of the VLS mechanism is that the growth species are firstly dissolved in the liquid catalyst droplet and then precipitate from it to form a nanostructure. Normally, the catalyst particle remains at the apex after growth in VLS. In contrast, in VS mechanism, the growth species directly form the nanostructures from vapor phase to solid phase. As a result, the presence of a catalyst particle after growth is an indication of VLS. In Vapor-solid-solid (VSS) mechanism, the growth temperature is lower than the eutectic temperature of the catalyst alloy which remains in solid phase.

These mechanisms have brought great achievements which will be reviewed in detail in Chapter 2.

1.2 Motivations

To rationally control the morphology of as-fabricated nanostructure is one of the most important goals in the nanostructure growth, because it can scale up the assembly of electronic devices. Generally, the morphology and growth behaviors of nanostructure are determined by the growth conditions, the substrate orientations, and the growth species. Lots of interesting nanostructures like nanowires (NWs), nanorods (NRs), nanobelts (NBs), nanotubes (NTs), nanotrees, nanoflowers, graphene and graphene-liked materials have been demonstrated. However, the growth mechanism is still not fully understood. Particularly, the correlation between the growth of vertical/planar NWs and the growth conditions has not been fully revealed.

Meanwhile, a post-growth assembly step is usually required to integrate nanostructures into electronic devices. One way to avoid this assembly step is to precisely control the position of the planar nanostructures. Till now, growth of planar nanostructures is still challenging. As a result, to develop a simple way to grow planar nanostructures is an emerging and important topic.

Furthermore, the growth mechanism of planar nanowires is less understood. Several reports have demonstrated the validity of the Gibbs-Thomson (G-T) effect in free-standing nanowires. However, the validity of G-T effect in planar nanowires, which can both advance the VLS growth mechanism and benefit the assembly of nanowire-based devices, has not been reported yet.

At last, the nanowire growth direction is an important topic in the bottom-up approach because it directly determines the morphology of as-grown nanostructures.

To manipulate the nanowire growth direction is always a difficult task. Some papers reported the growth direction manipulation by means of changing the reactant species concentration in the liquid catalyst, the growth temperature and pressure, and the type of reactant species. However, all these reports focused on the IV and III/V materials systems. The growth direction manipulation in oxide material systems has not been reported. As we know, oxide materials are important types of materials which own the interesting properties of wide band gap, high transparency, high UV sensibility, high stability in oxide environment and high crystallinity. Therefore, the growth direction manipulation of oxide materials is important topic to be studied.

In summary, the fundamental growth mechanism and the rational design of oxide semiconductor nanostructures are still challenging. The motivations of this research are to advance the study of the VLS growth mechanism and the rational growth of oxide semiconductor nanowires.

1.3 Outline of the Thesis

Chapter 1 gives an overview of the development of nanoscience and nanotechnology, and introduces the current challenges in nanowires research.

Chapter 2 gives a background on semiconductor nanowires growth. A literature review based on the growth mechanism is given.

Chapter 3 introduces the experimental procedures and the corresponding characterization techniques like scanning electron microscope (SEM), atomic force microscopy (AFM), electron beam lithography (EBL), (scanning) transmission

electron microscopy (STEM), and x-ray diffraction (XRD).

Chapter 4 introduces the rational control of the growth orientations in ITO NWs. In this chapter, the vertically, laterally and randomly oriented NWs are fabricated and measured in detail.

Chapter 5 introduces the direct observation of the Gibbs Thomson effect in the growth of planar NWs. Our results show that the growth speed of as-fabricated planar NWs conforms to the Gibbs Thomson effect in spite of their complicated growth orientations and morphologies.

Chapter 6 deals with the phenomenon of size-dependent growth direction. A novel nanocone-nanowire kinked structure is demonstrated and its crystal structure is studied in detail.

Chapter 7 summarizes the results and gives a review and outlook for the applications of nanowires.

Chapter 2. Synthesis of Nanowires

2.1 Growth Mechanisms

The most common growth mechanism for nanowires (NWs) is the vapor-liquid-solid (VLS) process which was first proposed by Wagner and Ellis in 1964.⁵ The concept is illustrated in Figure 2-1. The catalyst particle works as a reservoir and adsorbs the growth species vapor. When the catalyst nanoparticle gets supersaturated, the growth species will precipitate from it and form nanowires. An important feature of the VLS process is that the catalyst is liquid phase at the growth temperature which greatly reduces the growth energy barrier compared to the vapor-solid (VS) process. After several decades of development, the basic concept of VLS is still the same. But various *in-situ* techniques like *in-situ* electronic microscopy have revealed more details for the VLS mechanism. For example, Kim *et al* reported that the nucleation required a higher supersaturation level than the precipitation with the existing nucleus and observed a jumping growth speed between nucleation and steady growth.^{6,7} Normally, the growth species diffuse through the liquid catalyst to reach the growth front of a NW, but Sang *et al* reported that oscillatory growth and dissolution reactions at the top rim of the nanowires occurred and supplied the oxygen required to grow a new (0006) sapphire layer.⁸ Miroslov *et al* reported the direct observation of Au catalyst oscillation during the growth of Ge NWs.⁹

In VLS growth, the diffusion of the catalyst is often observed which is due to the limited solubility of catalyst in the NW and the Oswald ripening (Due to the Gibbs Thomson effect, the catalysts with big diameter have higher chemical potential than

that with small diameter, resulting in the disappearance of the small particles, which is called Oswald ripening). This conclusion is based on the observation of disappearance of the catalyst.¹⁰ No one has observed Au diffusion till Jonathan and co-authors used high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) to directly observe the gold migration on the sidewall of Si NWs.¹¹ The results are shown in Figure 2-2. Meanwhile Hanon and co-authors reported that the migration of Au can be prohibited by introducing low pressure oxygen.^{10,12}

Figure 2-1. Growth of Si NW via a VLS Growth Mechanism. Taken from Ref. 5.

The vapor-solid (VS) growth is another common method to fabricate NWs. Normally, in the VLS growth process, the catalyst is not the same materials as the growth species, so the catalyst can contaminate the as-grown NWs. Compared to VLS, the VS growth doesn't need the catalyst, so it can eliminate such contamination. The drawbacks of the VS process are that the nucleation barrier is higher than that in the VLS process, and the growth behavior is more difficult to control. ZnO NWs are very easy to grow and is a good example for the VS growth process because of the

large growth speed difference for c-axis and a- or b-axis. Woong *et al* reported the catalyst-free growth of ZnO NWs by metal-organic chemical vapor deposition (MOCVD) and thermal evaporation.¹³ Sekar *et al* reported similar results by oxidization of Zn powders.¹⁴ An interesting topic in VS growth process is screw-dislocation-driven growth which has been demonstrated for many gorgeous structures like pine-tree-like nanostructures and chiral branched NWs.^{15,16}

Figure 2-2. Diffusion of Au atoms. (a) In situ UHVTEM image recorded during the growth of Si nanowires. Scale bar: 50 nm. Taken from Ref. 10. (b) Three dimensional localization of Au atoms in a Si NW. Scale bar: 5 nm. (c) Excess intensity of Au atoms indicated in (b) plotted as a function of focal depth. Taken from Ref. 11.

The major difference between VLS and vapor-solid-solid (VSS) is that in VSS the catalyst is solid phase at the growth temperature (Figure 2-3). Normally the VSS

growth temperature is lower than the eutectic temperature of the catalyst alloy.¹⁷ The low growth temperature makes VSS growth compatible with the standard industrial processes. Meanwhile, the diffusion rate of the growth species in the solid-phase catalyst is much slower than in the liquid-phase catalyst. Therefore, the growth of heterostructure with atomically abrupt interface is achievable.¹⁸ As shown in Figure 2-3, Pin *et al* reported that the growth rates of InAs NWs were different in VSS growth when using highly faceted Au particle and spherical Au particle catalyst, which was attributed to the different indium adsorption between faceted Au particle and spherical Au particle.¹⁹ Ann *et al* reported that both VSS and VLS growth mechanisms can be achieved and switched by adjusting the growth temperature.²⁰

Figure 2-3. (a-c) Real-time TEM records during the growth of Si nanowire when temperature was reduced from 570 °C to 503 °C. Taken from Ref. 18. (d-f) The morphology and average growth speed of InAs NWs catalyzed by spherical and faceted Au particle. Taken from Ref. 19.

2.2 Growth Control Strategies

Rational design of the position, structure and morphology of NWs is always a central theme in NWs growth.⁴ To date, lots of approaches have been reported on how to control the NWs growth behaviors. In this thesis, the major effort was spent to improve the control of NWs growth behavior. Here we review the earlier attempts in growth control of NWs.

Growth Direction: The growth direction of NWs is determined by several factors: substrate orientations, growth conditions (pressure, temperature) and catalyst properties (composition, size).²¹ Our group has demonstrated that [100]-oriented indium oxide NWs can be grown on [100]-oriented yttria-stabilized zirconia (YSZ) substrate while [111]-oriented indium oxide NWs can be grown on [111]-oriented YSZ substrate. Lugstein *et al* reported that the growth direction of Si NWs is a function of the total growth pressure, i.e. at a total pressure of 3 mbar, the NWs grow preferentially in the $\langle 111 \rangle$ direction; at a total pressure of 15 mbar, the NWs favor the $\langle 112 \rangle$ direction.²² Hyun *et al* obtained very similar results.²³ Nari *et al* reported the pressure-dependent growth direction in Ge NWs.²⁴ Furthermore, several papers reported the size-dependent growth direction. As shown in Figure 2-4, the larger-diameter nanowires grow in $\langle 111 \rangle$ and $\langle 112 \rangle$ directions while the smallest-diameter nanowires grow in $\langle 110 \rangle$ direction.²⁵⁻²⁷ Tevye *et al* reported that the GaN NWs grow along $\langle 1\bar{1}00 \rangle$ direction by using a gold-rich catalyst, while the NWs grow along $\langle 11\bar{2}0 \rangle$ when using nickel-rich catalyst.²⁸ Zhi *et al* reported similar results in InAs and InP NWs separately.^{29,30}

Figure 2-4. Diameter-dependent growth direction of Si NWs. (a-c) Schematic side view of $[110]$ -, $[112]$ - and $[111]$ -oriented NWs. (d) Number density as a function of diameter for different growth directions. (e) Schematic of free energy as a function of the radius of both $[110]$ and $[111]$ -oriented NWs. Taken from Ref. 26.

Structure: The structure of NWs can be controlled by changing the substrate orientation and the growth precursor ratio. Tevye *et al* demonstrated the structure control of GaN NWs by using different substrates. As shown in Figure 2-5, the $[110]$ -oriented GaN NWs with triangular cross-section grow on $\gamma\text{-LiAlO}_2$ (100) plane and the $[001]$ -oriented GaN NWs with hexagonal cross-section grow on MgO (111) plane.³¹ Caroff *et al* demonstrated the control of the Wurtzite/Zinc Blende ratio and the defect density in InAs NWs by changing the NW diameter and growth temperature.³²

This phenomenon is induced by the surface energy difference between Wurtzite and

Zinc Blende structures. Hanhah *et al* also found similar trends in GaAs NWs.³³ In addition, Rienk *et al* reported a new approach to switch the Wurtzite and Zinc Blende structures by Zn doping in InP NWs showing that higher Zn-doping favors Zinc Blende structure while lower Zn-doping favors the Wurtzite structure.³⁴

Figure 2-5. (a,b) SEM images of GaN NWs on (100) γ -LiAlO₂ and (111) MgO substrates, respectively. (c) Schematic illustrating the crystal structures of the substrate at the interface. Taken from Ref. 31. (d) TEM image of an InP NW. “On” means the segment is doped with Zn and “Off” means the segment is not doped. (e) Average segment length between two adjacent stacking faults as a function of the diethylzinc concentration. (f) Calculated kinetic phase diagram as a function of $\Delta\mu$ and $\Delta\gamma/\gamma$. Taken from Ref. 34.

Growth position: The growth position of NWs is directly determined by the position of the catalyst. There are several techniques to define the position of the catalyst, e.g. photolithography, e-beam lithography, and nanosphere lithography.

Photolithography and e-beam lithography are widely used because the pattern can be designed at will. In this thesis, we mainly use the e-beam lithography which will be discussed in Chapter 3. In this part, we just discuss the possible usage of nanosphere lithography. Nanosphere lithography is based on the self-organization of the nanosphere into a monolayer on the substrate surface, which is an economical and convenient approach. The nanosphere monolayer works as a mask. After deposition of the catalyst, this sacrifice nanosphere monolayer can be removed and then the catalyst pattern remains on the surface. This approach is able to produce hexagonal structure in a very large area. The drawback is that it can only provide catalyst with hexagonal structure due to the hexagonal close packing of the nanosphere. As shown in Figure 2-6, Bodo and co-authors demonstrated this approach to grow Si NWs.³⁵ In another paper, Fan *et al* slightly modified this approach and transfer the nanosphere monolayer to the GaN substrate to grow the ZnO NWs.³⁶

Figure 2-6. Steps of Si NWs fabrication through a nanosphere lithography approach. (a) Nanosphere self-assembly. (b) Au deposition. (c) Removal of the nanosphere. (d) Thermal annealing. (e) Si NWs growth. Taken from Ref. 35.

Complex Structures: Many complex structures like kinked structures,^{37,38} branched structures,³⁹ heterostructures,⁴⁰ nanorings⁴¹ and nanowebs⁴² have been demonstrated by modulating the growth parameters. As shown in Figure 2-7, these complex structures show the flexibility of the VLS method and enable the applications of the NWs in a broad field of research. For kinked structures, Lieber *et al* introduced a stepwise synthesis method to fabricate kinked semiconductor superstructures.⁴³ The growth sequence of such superstructure is as follows: axial growth, suspended nanowire elongation, and axial growth (second building unit). Shin *et al* reported that adsorbed hydrogen atoms were responsible for the switch of growth direction in Si NWs.⁴⁴ For the branched NWs, Lieber *et al* introduced a multistep nanocluster-catalyzed process to fabricate branched and hyperbranched nanostructures.^{45,46} A NWs trunk is firstly grown, then Au nanoclusters are deposited on the NWs, finally the first order branches are grown. Wang *et al* reported the growth of ZnO with nanowires-nanoribbon junction arrays by using the mixture of ZnO and SnO₂ powder via a thermal evaporation approach.⁴⁷ Samuelson *et al* reported the fabrication of nanotrees by using sequential seeding of branching.³⁹ M. Jacobson *et al* used an ion beam technique to deposit Au catalysts on the trunk of nanowires and controlled the growth of the second wire segments.⁴⁸ Regarding NW heterostructures, Lieber and co-authors reported the fabrication of modulation-doped Si NWs and demonstrated their applications in photovoltaic devices.⁴⁹⁻⁵¹ Vomiero *et al* modulated the catalysts and grew radial and longitudinal heterostructures of indium oxide and tin oxide.⁵²

Figure 2-7. (a,b) Schematic and SEM image of coherently multiply kinked nanowire and the secondary building units, respectively. Taken from Ref. 43. (c,d) Schematic and SEM image of the branch NWs. Taken from Ref. 45. (e,f) Schematic and SEM image of two p-i-n tandem axial Si NW integrated in series on a single NW. Scale bar 1 μm . Taken from Ref. 50.

2.3 Gibbs-Thomson Effect in NWs Growth

The size-dependent growth speed in the semiconductor nanowires is generally described by the well-known Gibbs-Thomson (G-T) effect which claims a reduction of the supersaturation, the driving force for growth, when the size of nanowires decreases. The G-T equation is derived from the Gibbs free energy as follows.

Figure 2-8. Schematic illustrating the Gibbs-Thomson effect.

As shown in Fig. 2-8, when the length of NWs increase ΔL , the increases of Gibbs energy is given as,

$$\Delta G = -\Delta\mu_0 \times \Delta N + \Delta S \times \sigma_{vs}$$

where $\Delta\mu_0$ is chemical potential with infinite radius of curvature, ΔN is increased number of atom, σ_{vs} is surface energy. We know the volume and surface increases are given as,

$$\Delta V = \pi \times \left(\frac{d}{2}\right)^2 \times \Delta l$$

$$\Delta S = \pi \times d \times \Delta l$$

So, the atom number increases is,

$$\Delta N = \frac{\Delta V}{\Omega} = \frac{\pi \times \left(\frac{d}{2}\right)^2 \times \Delta l}{\Omega}$$

where Ω is atomic volume. As we know, the chemical potential is defined as

$$\Delta\mu = -\frac{\Delta G}{\Delta N}$$

We substitute ΔV , ΔS and ΔN in ΔG and obtain the G-T equation:

$$\Delta\mu = \Delta\mu_0 - \frac{4\Omega\sigma_{vs}}{d}$$

Normally, the NWs growth speed is determined by an empirical quotation,

$$v = b \left(\frac{\Delta\mu}{kT} \right)^2$$

where k is Boltzmann constant, T is absolute temperature, b is kinetic coefficient. We substitute the chemical potential and obtain the dependence between the growth speed and the diameter of nanowire as follows:

$$\sqrt{v} = \sqrt{b} \frac{\Delta\mu}{kT} = \sqrt{b} \times \frac{\Delta\mu_0}{kT} - \sqrt{b} \frac{4\Omega\sigma_{vs}}{kT} \times \frac{1}{d}$$

This is the G-T equation in NWs growth.

Givargizov is the first to experimentally reveal the G-T effect in the vapor-liquid-solid (VLS) growth of Si microwires about four decades ago and verify the quadric dependence of their growth velocity on supersaturation.⁵³ Recently, Dayeh *et al* reported the direct observation of G-T effect in the vertical Ge nanowires and verified the G-T equation quantitatively.⁵⁴ Their results support the universal applicability of the Gibbs-Thomson effect to sub-100 nm diameter semiconductor NW growth. Biswas *et al* used bimetallic alloy seeds of $\text{Au}_x\text{Ag}_{1-x}$ to enhance the growth kinetics of Ge nanowires and established the correlation between the growth kinetics and equilibrium eutectic compositions in this ternary growth systems.⁵⁵ Lee *et al* reported the growth of ZnO nanowire through a solution-phase also conforms to G-T effect and proved that the Gibbs-Thomson effects are universally applicable to a variety of material systems.⁵⁶

Figure 2-9. (a) SEM images of vertical Ge NWs grown for 15 min from randomly dispersed Au colloids of nominal diameter 10, 20, 30, 40, 50, 60, 100, and 250 nm. (b) Plot of the NW length as function of diameter for different growth. Taken from Ref. 54. (c) Growth rate distributions with different catalyst systems. (d) Plots of the quadratic dependence of the growth rate with nanowire diameter grown with three different seeds. Taken from Ref. 55. (e) SEM images of ZnO hexagonal rod arrays with different D_{ZnO} . (f) Plots of H_{ZnO} versus D_{ZnO} for the ZnO hexagonal rod. Taken from Ref. 56.

Chapter 3. Experimental Methodology

3.1 Synthesis of Oxide Nanowires

3.1.1 VLS Growth of ITO NWs

In Chapter 2, we reviewed the different approaches to grow nanowires (NWs). In this research, we used chemical vapor deposition (CVD) method to grow NWs *via* a vapor-liquid-solid (VLS) mechanism in home-built thermal evaporator system. The obvious advantages of this system are the low cost, ease of operation, high flexibility and high throughput. The typical system is composed of a mechanical pump, a furnace, a quartz tube, a mass flow controller, a pressure gauge, a gas cylinder and the connectors between every component. Figure 3-1 shows the schematic of our system. The source, which is a mixed powder of the growth species, is located at the center of furnace. The substrate is placed several centimeters away from the source in the downstream side of the gas flow. The growth pressure inside the quartz tube is modulated by the gas flow speed and the valve of the mechanical pump. The growth temperature is set by the furnace, with highest temperature up to 1200 °C. The temperature along the furnace is calibrated by a thermocouple.

A typical growth for ITO NWs is carried out as follows. The source is a mixture of $\text{In}_2\text{O}_3/\text{SnO}_2/\text{C}$ with weight ratio of 0.6:0.4:1 and total weight of 0.05g. The yttria-stabilized zirconia (YSZ) substrate is cleaned with acetone and ethanol for 10 minutes and then coated with 1 nm Au by sputter. Thus the YSZ substrate is placed 9 cm away from the source. The Ar gas flow speed is set at 100 sccm and the pressure inside the tube chamber is maintained at 30 mbar. The furnace is heated up to 900 °C in 18 mins

with a ramping speed of 50 °C/min. After 30 mins growth, the furnace is turned off and the delivery gas is shut down immediately. The sample is taken out at room temperature. At the growth temperature of 900 °C, the source generated indium and tin vapor. The chemical reaction equations are given by:

The indium and tin vapors are delivered to the substrate surface by Ar carrier gas. The Au catalyst adsorbs the indium and tin vapors to form a liquid alloy droplet. When it becomes supersaturated, the indium and tin precipitated from the liquid catalyst droplet and react with O₂ to form the ITO NWs. Because the contaminated O₂ in air is enough for the growth, we didn't add O₂ intentionally.

Figure 3-1. Schematic of the furnace set-up (not drawn to scale) and the temperature profile inside the furnace, calibrated with a thermocouple. Two typical growth temperatures, 800 °C and 900 °C, were calibrated.

The representative morphologies of as-grown ITO NWs are shown in Figure 3-2. Because of the small mismatch of the ITO crystal and the YSZ crystal, the ITO NWs are vertically aligned on the YSZ substrate. Conversely, the ITO lattice doesn't match the SiO₂ lattice, so the ITO NWs are randomly oriented on the SiO₂ substrate. In spite of differences in their growth orientations, the catalyst particles at the apex of the ITO NWs are easily observed, suggesting the VLS growth mechanism.

Figure 3-2. (a) ITO NWs on YSZ substrate. The ITO NWs are vertically aligned. (b) ITO NWs on SiO₂ substrate. The ITO NWs are randomly oriented. Scale bar: 1 μm.

3.1.2 Electron Beam Lithography (EBL) Patterning

Normally, an Au film is used as the catalyst. Au nanoparticles are formed when annealing the thin film at growth temperature. The advantage of this method is its simplicity and the drawback is that the NWs position can't be controlled. In order to control the position where the NWs grow, we used electron beam lithography (EBL) to define the Au catalyst position. A typical EBL procedure is as follows:

- 1) Coat the substrate with PMMA by a spin coater at the speed of 4000 rpm for 45s. The resulting thickness of the PMMA film is about 200 nm.
- 2) Bake the substrate at 180 °C for 5 mins.

- 3) Load the substrate inside the EBL chamber and complete the electron beam exposure. Typical charge density during exposure is $100 \mu\text{C}/\mu\text{m}^2$ at 10 KV.
- 4) After exposure, develop the substrate with MIBK:IPA (1:3 wt%) solution for 30s at room temperature and rinse with IPA for 30s.

The pattern of the Au catalyst is designed by the computer software “**E-Line**”. The size of the Au discs varies from 100 nm to 800 nm based on requirements.

3.1.3 Au deposition

After EBL patterning, we deposit the gold film with a thickness of 20 nm by e-beam evaporation system. A layer of Ti with thickness of 2 nm was coated before the Au film to enhance adhesive. Then, the substrate was developed in acetone for several hours. The unwanted Au was washed away and the catalyst pattern remained on the substrate surface.

The working principle of e-beam evaporation is using high speed electrons accelerated by a 5KV electric field to hit the target and heat up it until target vapor is generated. The target vapor flows to the substrate and is deposited on substrate surface. A thickness monitor is located near the substrate to monitor the thickness of the metal film in real time during deposition. Figure 3-3 illustrates the basic components of an e-beam evaporation system

Figure 3-3. Schematic of the e-beam evaporation system.

In summary, ITO NWs presented in this thesis grow *via* the VLS process. The position of NWs is controlled when pattern Au discs are used as catalyst. Figure 3-4 shows the experimental work flow, from EBL patterning to NWs growth.

Figure 3-4. Schematic illustrating the experimental work flow for NWs growth.

3.2 Characterization Techniques

3.2.1 Scanning Electron Microscope (SEM)

SEM is the most frequently used equipment in materials research. The capability of high resolution ($\sim$ nm) and ease of operation make it the important characterization tool for nanomaterials. The first commercial SEM was invented in 1965. Since then, the performance of SEM has been dramatically improved. Nowadays, environmental SEM (ESEM) is capable to observe living biological samples at atmospheric pressure.

The working principle of SEM is to collect the secondary electron signal after injecting a high energy electron beam into the specimen surface. Figure 3-5 shows the working principle of an SEM and the veils of electron-specimen. In Figure 3-5, we can note several factors affecting the SEM imaging:

- (1) **Cathode.** The cathode used to be made of tungsten filament which has obvious disadvantages, like unstable current and short lifetime. In modern SEM systems, the cathode composes of field emission gun which can overcome these drawbacks.
- (2) **The electron lens.** The electron lens should be properly adjusted to eliminate or minimize spherical aberrations and chromatic aberrations of the electron beam yields.
- (3) **The accelerating voltage.** High accelerating voltage yields higher electron speed and generates more signals, but the drawback is the loss of the information about the substrate surface, and slight reduction of the resolution.
- (4) The angle between the incident electron beam and the specimen surface should

be minimized. When the incident electron beam is not perpendicular to the specimen surface, more electrons can escape from the specimen, which will increase signal intensity but decrease resolution. This is why the edge of the sample is usually brighter than the body in SEM observation.

Figure 3-5. Schematic illustrating the working principle of a SEM system. (a) The schematic of SEM equipment. (b) The interaction between the incident electron beam and the substrate. (c) Penetration depth of incident electron beam (top) and X-ray excitation (bottom) on different materials, at an accelerating voltage of 20 kV.

Usually, there are two modes of operation of the SEM, based on which way the electron signal is collected. In the secondary electron mode, one detects the second electrons, while in the back scattered mode one detects the back scattered electrons. Their differences are the following: (1) Back scattered mode needs higher operation voltage, therefore has less resolution. (2) Back scattered mode is more sensitive to the composition of the specimen.

3.2.2 Energy Dispersive X-Ray Spectroscopy (EDS or EDXS)

EDS is an elemental analysis technique. It is usually integrated in a SEM or TEM system. The working principle of EDS is shown in Figure 3-6. One incident electron excites one electron in the inner shell to vacuum and creates a hole in the specimen atom. Then an electron from the outer shell will fill this hole and emit x-rays. The x-rays are collated by a detector. The frequency of x-rays is determined by the energy difference between the higher energy shell and the low energy shell. The energy of x-rays reveals the energy difference between the shells in an atom, so it allows determination of the elements present in the substrate.

Figure 3-6. Schematic illustrating the working principle of EDS.

Because the intensity of x-rays is dependent on the yield of inner holes, higher accelerating voltage will generate more signals and obtain more accurate spectrum. Due to the window of absorption of x-rays at low energy region, EDS cannot detect light weight atoms such as H, He, Li, P and B. In addition, some elements have overlapping peaks, such as Ti K_{β} and V K_{α} , so they are not distinguishable.

3.2.3 X-Ray Diffraction (XRD)

XRD is a non-destructive analytical technique to study the lattice constant and

grain size of crystalline materials. Because different materials have different crystal lattice, it is used to determine the materials composition. The working principle of XRD is illustrated in Figure 3-7, when the wavelength of x-rays is comparable to the crystal lattice constant (0.01 ~ 10 nm), they will be diffracted by the crystal. The diffraction equation is given by Bragg's law:

$$n\lambda = 2d \sin\theta$$

where n is an integer determined by the order of diffraction, λ is the wavelength of the X-rays, d is the plane spacing in the atomic lattice, and θ is the angle between the incident ray and the scattering planes. Normally, one knows the value of λ , so he can determine the value of d .

Figure 3-7. (a) Photography of the D8 Powder XRD instrument available in our lab. (b) Schematic illustrating the working principle of XRD.

The mechanism of x-ray generation is very similar to the working principle of EDS discussed in the last section. The electron beam accelerated by high voltage (40 kV) hits the target and the target emits x-rays simultaneously. Normally, we use Cu as target materials for which the emitted x-rays wavelength locates at 1.54 nm. For some special applications, one can also switch the Cu to Cr (2.29 nm), Fe (1.94 nm), Mo

(0.71 nm) and Ag (0.56 nm). From the diffraction equation, one can determine the d values, characteristic of different materials. By comparing these d values to standard diffraction databases, one can finally determine the composition of materials.

Moreover, the grain size of polycrystalline materials can be derived by the Scherrer equation:

$$\tau = K\lambda / \beta \cos\theta$$

where τ is the mean size of crystalline domains, K is the shape factor with a typical dimensionless value of ~ 0.9 , λ is wavelength of the X-ray, β is FWHM value, and θ is the angle between the incident ray and the scattering planes.

3.2.4 Reciprocal Space Mapping (RSM)

The working principle of reciprocal space mapping (RSM) is similar with the common XRD. The advantages of RSM over XRD are that RSM can give more information about the crystal twinning, strain, and defects.

Fig. 3-8a illustrates the working principle of RSM. If the lattice arrays in reciprocal space touch the Ewald's sphere, a diffraction peak will be detected according to the Bragg's law. If the crystal is distorted (Fig. 3-8 a-c), the lattice arrays in reciprocal space also change (see the black and red dot arrays in Fig. 3-8a). The consequence is that the Ewald's sphere will touch the lattice arrays at different position and the diffraction peaks will appear in different position during mapping, even though the plane indexes are the same for non-distorted crystal and distorted crystal. RSM is an important technique to study the structure properties of a thin film epitaxially grown

In the normal XRD measurement, one does a θ - 2θ scan (single line scan). The sample stage is fixed. The x-ray generator and the detector rotate simultaneously and collect the diffraction signal intensity against θ . In RSM, as shown in Fig. 3-8d-f, the substrate stage is rotated in a small range, which allows one to obtain a gradient signal in the reciprocal space. The RSM is very sensitive to the slightly lattice distort/twist inside the crystal.

TEM is a powerful tool to examine the materials structure in details with an extremely high resolution (~ 0.1 nm). As shown in Figure 3-9, a TEM is very similar

to SEM in section 3.2.1. The major difference is that the detector in TEM collects the transmission electron signals while the detector in SEM collects the secondary electron or back scattered electron signals. The TEM is usually operated at very high accelerating voltage (100~300 kV) while the SEM is operated at relatively low accelerating voltage (standard: 10 kV).

The interaction between incident electron and sample is similar to the case of XRD. The incident electron is diffracted by the periodic atoms in the sample and the diffraction equation gives as:

$$n\lambda = 2d \sin\theta$$

where n is an integer determined by the order, λ is the wavelength of the electron wave, d is the plane spacing in the atomic lattice, and θ is the angle between the incident electron beam and the scattering planes. Normally θ is very small, so $\sin\theta \approx \theta$.

Therefore, we can get: $n\lambda = 2d\theta$.

Figure 3-9. (a) Schematic of TEM equipment. (b) The working principle of selective area electron diffraction (SAED) measurement.

The wavelength of electron wave is dependent on the electron kinetic energy E . As we know, the acceleration voltage in TEM is so high that the velocity of electron is near the speed of light. We should then consider the relativistic effect. Therefore, the wavelength of electron wave is given as:

$$\lambda_e = \frac{h}{\sqrt{2m_0E \left(1 + \frac{E}{2m_0c^2}\right)}}$$

where h is Planck's constant, m_0 is the rest mass of an electron, E is the electron kinetic energy, and c is the speed of light. For a typical TEM equipped with a 100 keV electron source, the wavelength of electron is ~ 4 pm ($1 \text{ pm} = 10^{-12} \text{ m}$). The wavelength of electron is four orders smaller than x-rays, so TEM has much higher resolution than XRD.

Compared to SEM and XRD, the drawback of TEM is the strict requirements for sample preparation. Because incident electrons are transmitted through the sample, the thickness of the sample should be very small ($< 1 \text{ }\mu\text{m}$). This requirement makes sample preparation is very challenging and somehow limits its application.

3.2.6 Scanning Transmission Electron Microscopy (STEM)

The working principle of a STEM is similar to the conventional TEM described in the last section, and the STEM is a type of TEM in fact. The feature of the STEM is that the electron beam spot size is focused into an extremely narrow spot ($\sim 1 \text{ }\text{\AA}$) which is smaller than the atomic diameter, so it is possible to form atomic resolution images. The conventional TEM uses phase-contrast technique to image the specimen. However, in STEM, the contrast of image is related to the atomic number (z-contrast

image).

Normally, the resolution of conventional TEM is limited by aberration, especially the spherical aberration (Cs). To improve the resolution in STEM, the spherical aberration is corrected (Fig. 3-10a). After Cs-correction, the electron beam is coherently convergent.

As shown in Fig. 3-10b-d, there are different operation modes (detectors) in STEM system, i.e. bright field (BF), annular dark field (ADF), and high angle annular dark field (HAADF).

BF detector is placed at the same site as the aperture and detects the intensity in the direct beam from a point on the specimen, while the ADF detector is a disk with a hole in its center where the BF detector is installed. The ADF detector uses scattered electrons for image formation, similar to the DF mode in TEM. The measured contrast mainly results from electrons diffracted in crystalline areas but is superimposed by incoherent Rutherford scattering. The signal collection efficiency is very high in the ADF detector.

The HAADF detector is a disk with a hole, but the disk diameter and the hole are much larger than that in the ADF detector. Thus, it detects electrons that are scattered to higher angles and almost only incoherent Rutherford scattering contributes to the image. As opposed to Bragg scattered electrons in conventional TEM, The HAADF detector is highly sensitive to variations in the atomic number of atoms in the sample (Z-contrast images). Therefore, the HAADF is capable to distinguish the adjacent atoms.

Figure 3-10. (a) Schematic of a lens with and without spherical aberration (Cs). (b) Schematic illustrating the different operation modes or detectors in a STEM system. (c-d) Schematic illustrating the bright field image and the dark field image.

3.2.7 Atomic Force Microscopy (AFM)

The AFM is a convenient tool to measure the surface topography of a sample. Compared to SEM, AFM can provide more details about the surface profile with a height resolution of 0.1 nm. Figure 3-11 shows the working principle of AFM. AFM is operated based on the interaction force between the substrate and the cantilever tip. Generally, there are two different forces, the repulsive and the attractive forces between the tip and the substrate surface depended on their distance. In operation, a laser beam is shone to the top surface of the tip and the reflected light is detected by a

photodetector. When their distance is, i.e. larger than the equilibrium distance, the AFM tip is attracted to bend down, resulting in the decreases of the detected light intensity. A piezoelectric ceramics in where the AFM cantilever mounted will increase the tip-substrate distance simultaneously to maintain the detected light intensity. The height profile of substrate surface is consistent with the length changes of the piezoelectric ceramics.

AFM has two different operation modes, the contact mode and non-contact mode. In contact mode, one measures the repulsive force. In the non-contact mode, one measures the attractive force. If the stiffness of the substrate surface is high, contact mode is a better operation. If the substrate is an elastomer, non-contact mode provides better results.

Figure 3-11. Schematic illustrating the working principle of an AFM system. (a) The schematic of AFM equipment. (b) The interaction force between the tip and the substrate based on their distance (z-value). (c,d) Schematics showing some limitations in AFM mapping.

AFM has some limitations: (1) The detection depth is limited to several micrometers ($\sim\mu\text{m}$) and the scan size is limited to $\sim 100\ \mu\text{m} \times \sim 100\ \mu\text{m}$. (2) The scan speed is also slow, limited by the piezo stage response speed.

Chapter 4. Growth Orientation Control in Oxide Nanowires

4.1 Introduction

Since the first report of the vapor-liquid-solid (VLS) growth mechanism in 1964 by Wagner and Ellis,⁵ there have been lots of important works developing nanowires (NWs) synthesis and applications.^{16,54,57,58} Because NWs have high surface-volume ratio and other promising properties,^{4,59} they have been intensively explored for a wide range of applications in electronics,⁶⁰ photonics,⁶¹ chemical/biological sensing^{1,62,63} and energy harvesting/conversion.^{34,64,65} However, it is very challenging to incorporate the as-grown out-of-plane NWs into nanodevices which often have planar configurations in a large scale with high-precision. Normally, the representative fabrication approach separates the NW growth and assembly steps. For example, the as-grown NWs were firstly dispersed in a solution and then were casted on substrates. Several strategies such as the Langmuir-Blodgett technique,⁶⁶⁻⁶⁸ blown-bubble method,⁶⁹ micro fluidic alignment,⁷⁰ and micro-contact printing^{71,72} have also been reported to solve this issue of NW assembly. However, these approaches will bring new problems like imperfect alignment, mechanical damage, and solution contamination.

Recently, there are reports on the self-assembled growth of planar NWs. These planar NWs can be directly integrated into devices which can eliminate the assembly step in fabrication.⁷³⁻⁸² However, there is a stringent requirement in this approach which is good lattice match between NW and substrate so that only limited examples are fabricated successfully in the literature. Majority of the previous reports regards

wurtzite (hexagonal)-structured II-VI semiconductors, such as ZnO NWs on sapphire⁷⁴ or GaN,⁷⁷ and GaN NWs on sapphire⁷⁹ or SiC.⁸¹ Recently, some reports emerged on synthesis of planar III-V semiconductor NWs with Zinc Blende (cubic) structures, such as GaAs NWs on GaAs,⁷⁵ and InAs NWs on GaAs.⁷⁶ Furthermore, self-aligned lateral NWs of In₂O₃, which is an important wide band gap oxide, was reported to grow on Si substrates.⁷³ However, the In₂O₃ NWs exhibited a semiellipsoidal cross section, indicating that the lattice mismatch as high as 7% and the SiO₂ layer at the In₂O₃/Si interface might compromise the synthesis of high quality NWs. Regarding the growth mechanism, Zi and coworkers recently used a revised Gibbs-Thomson equation to illustrate that growth of planar InAs NWs is energetically favored at lower vapor pressure and smaller NW diameter.⁸³ On the dynamic aspect, Schwarz and Tersoff developed an anisotropic continuum model to capture the interplay between droplet statics and facet formation, and they successfully explained the anomalous kinking and crawling phenomena often observed in NW growth.⁸⁴⁻⁸⁶

In this chapter, we demonstrate that growth epitaxy and thermodynamics can be utilized to enable unprecedented control of the orientations and morphologies in tin-doped indium oxide (ITO) NWs. ITO NWs have widely applications for solar cells, displays, plasmonics and LED because of their simultaneous high transparency and conductivity,⁸⁷⁻⁹⁷ In the previous works,⁸⁸⁻⁹⁷ several groups have reported the transparent conducting nature of random and vertically aligned ITO NWs and demonstrated the applications. In this thesis, we report a simple yet reliable method to

grow not only random and vertically aligned ITO NWs, but also planar ITO NWs on yttria-stabilized zirconia (YSZ) substrates by controlling the growth temperature profile. We use high-resolution transmission electron microscopy (HRTEM), electron diffraction (ED), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), annular bright-field STEM (ABF-STEM) and x-ray diffractometry (XRD) to investigate the structural properties of the as-fabricated ITO NWs. The epitaxial relationship between the ITO NWs and the YSZ substrate are revealed. This epitaxial relationship enables a variety of ITO nanostructures with rich symmetry, orientation, and morphology. Our results bring insights in the general VLS mechanism for NW growth, opening doors for the production of novel nanoscale architectures and devices.

4.2 Experiments and Results

4.2.1 Experimental procedures

ITO NWs were grown on YSZ substrates using the vapor transfer deposition growth process in a horizontal furnace with controlled gas delivery and pumping. A mixture of In_2O_3 , SnO_2 and graphite powder with weight ratios of 0.6:0.4:1 was used as the source. This mixture was put at the center of the furnace quartz tube. YSZ substrate was cleaned by acetone and ethanol for 10 mins and then was coated with 1 nm Au thin films by sputtering. YSZ substrate was located about 9 cm downstream from the source. Argon gas was introduced as the delivery gas to transfer vapor from the source to the substrates. The gas flow was kept at 10 sccm (standard cubic

centimeters per minute) and the pressure inside the tube was fixed at 1 mbar during NW growth. The ramping rate of the furnace was fixed at 50 °C/minute and the temperature overshoot was smaller than 5 °C. After growth, the argon gas was shut down immediately and the furnace was cooled down naturally.

To obtain patterned catalysts, 4% 950K PMMA in Anisole (950 A4, MicroChem, Inc.) was spin-coated on YSZ substrates (4000 rpm, 45 s). The thickness of PMMA film is ~200 nm. The pattern was designed and written on a Raith E-line system with a highest electron acceleration voltage of 30 KV. After pattern writing, the substrate was developed in a MIBK:IPA (3:1) solution for 30 s and rinsed in IPA solvent for 30 s. At last, Ti (2 nm) and Au (20 nm) bilayers were deposited by electron beam evaporation, followed by a standard lift-off process in acetone. The subsequent NW growth process is similar to the unpatterned case.

The morphology of the ITO NWs was examined by field emission scanning electron microscopy (FESEM, JEOL JSM-6700F). The conventional θ -2 θ XRD investigations on the structure of as-made NWs were done on an x-ray diffractometer (Bruker D8, $\lambda=1.54184$ Å). The high-resolution RSM data of planar and vertical NWs were collected at the X-ray demonstration and development (XDD) beamline in the Singapore Synchrotron Light Source (SSLS, $\lambda=1.5404$ Å) and the diffractometry station at the Shanghai Synchrotron Radiation Facility (SSRF, $\lambda=1.2398$ Å). Cross-sectional samples for TEM investigation were prepared using a FEI Helios FIB-SEM instrument. High-resolution TEM (HRTEM) imaging and electron diffraction (ED) were carried out on a FEI Tecnai G2 30 UT transmission electron microscope

operated at 300KV. (HA)ADF-STEM and ABF-STEM images were acquired on a FEI Titan 80-300 “cubed” microscope fitted with an aberration-corrector for the probe forming lens, operated at 300 kV.

4.2.2 In-plane, out-of-plane and randomly oriented ITO NWs grown on (100) substrates

The typical growth conditions and corresponding scanning electron microscopy (SEM) images of as-fabricated NWs on (100)-oriented YSZ substrates are shown in Figure 4-1. In Figure 4-1a, the temperature profile shows the two-step approach to grow in-plane NWs. We first quickly raised the furnace tube to 900 °C, and stayed at 900 °C for 10 minutes. Then we lower the furnace temperature to 800 °C at a controlled rate of 10 °C/min. The whole growth process including the cooling down to room temperature takes roughly 1.5 hours. Figure 4-1d,e show the corresponding SEM images of as-fabricated planar NWs. Au nanoparticles at the apex of NWs can be clearly identify which indicates that the NW growth follows the VLS mechanism. As shown in Figure 4-2, XRD patterns confirm that these NWs are ITO with the cubic bixbyite crystal structure. Importantly, the orientations of the planar NWs show four-fold symmetry, which is a direct result of the epitaxial crystallographic relationship between ITO NWs and YSZ substrate. This epitaxial relationship is confirmed by TEM characterizations. As we know, YSZ is an ideal substrate for the growth of ITO NWs. Because YSZ is a cubic structure and has small lattice mismatch with ITO which is as small as 1.6%. As a result, the interface energy between ITO NWs and

YSZ substrate will be the lowest when the ITO NWs grow epitaxially along specific [010] and [001] directions on the (100) YSZ surface. In the SEM images in Figure 4-1e, we found that many tiny isolated Au particles with diameters smaller than 30 nm were still present on the substrate surface. These Au nanoparticles are likely too small to initiate the NW growth due to the Gibbs-Thomson effect.⁵³ Overall, the planar ITO NWs exhibit a width of 50 ± 9 nm, whereas the length has a much wider distribution between approximately 335 and 635 nm.

Figure 4-1. Synthesis of ITO NWs on (100) YSZ substrates. (a-c) Schematic illustration of the dynamic temperature profiles used in the synthesis of planar, vertical and random NWs, respectively. (d-i) SEM images of planar, vertical and random NWs at different magnifications, respectively. Scale bars: 1 μ m in (d), (f-h), 100 nm in (e), (i) and insets in (f),(g).

In Figure 4-1b, a single growth temperature of 800 °C was used during a growth time of one hour. Such growth conditions for vertically aligned ITO NWs are consistent with previous reports.⁸⁹⁻⁹¹ The SEM top-view image in Figure 4-1f suggests square-shaped cross sections for the NWs with a uniform width of about 140 ± 18 nm and length of 980 ± 140 nm. The tilted view in Figure 4-1g shows that the ITO NWs exhibit a slightly tapered morphology and the Au nanoparticles are generally much smaller than the NW diameters, which is a result of the diffusion of Au catalyst during the VLS growth.⁸⁹

Figure 4-2. XRD data of vertical, planar and random nanowires grown under different growth conditions.

As shown in Figure 4-1c, when the growth temperature was further lowered to 750 °C, random NWs without any preferred orientation are obtained. In Figure 4-1h,i, the SEM images show that the NWs are no longer uniform and majority of the NWs

are not straight. The XRD data (Figure 4-2) indicate that the majority of the NWs have a rutile crystal structure that is consistent with SnO_2 , although some ITO NWs are still present. The reason of forming SnO_2 NWs is the fact that tin oxide can react with graphite and produce tin vapor at a lower temperature than indium oxide.⁹⁷ So the formation of SnO_2 NWs is favored under lower growth temperature. Since SnO_2 NWs have a rutile structure ($a = 4.750 \text{ \AA}$ and $c = 3.198 \text{ \AA}$), which does not match the structure of YSZ substrate (cubic, $a = 5.150 \text{ \AA}$), as a result, the growth of NWs is random. In addition, there is no NWs grow at 700°C and below which may be due to the limited reaction of the source mixture at low temperatures.

There are two immediate conclusions from the three runs of experiments: the first conclusion is that planar NWs will grow at the highest temperature, while NWs grow vertically at slightly lower temperatures, and randomly oriented NWs are obtained at the lowest temperature of 750°C ; the second conclusion is that two temperature steps are essential to fabricate planar NWs. This unusual growth process may be the reason why no one reported the growth of planar ITO NWs before. In order to better understand the growth process, we carried out about 100 runs of NW growth under systematic tuning of growth parameters, and the Figure 4-3 summarizes the effect of growth temperature on the NW morphology. For the growth of planar NWs, we fixed the temperature T_1 and T_2 at 900°C and 800°C , respectively; the time duration t_1 at T_1 was fixed at 10 minutes, while the transition time t_2 was changed from 5 to 40 minutes. We found that the length of the NWs is controlled by the duration t_2 , when the growth temperature is lowered from 900 to 800°C , and the length of the NWs is

controlled by the duration t_1 . On the other hand, when we fixed the temperature T_1 , T_2 and time t_2 , and changed t_1 , the length of NWs remained nearly the same, but the number of planar NWs decreased with t_1 . These results suggest that the planar NWs grow during the process of controlled cooling from 900 °C (T_1) to 800 °C (T_2). Without process t_2 , no NWs grow, which may be the result of the high decomposition/desorption rate of ITO in the reducing atmosphere at 900 °C.

Figure 4-3. Systematical illustration of growth conditions of ITO nanowires. (a) SEM images of nanowires fabricated under different growth conditions. (b) Schematic diagram of the general temperature evolution during the NW growth. T_1 is the highest temperature, and T_2 is fixed at 800 °C. (c) Schematic illustration of the results of different growth schemes. For the notations in (c), I: in-plane growth of ITO NWs; O: out-of-plane (vertical) growth of ITO NWs; R: random growth of NWs; N: no nanowires on substrate. In the first column where t_2 is zero, no NW grows at 700 °C and 900 °C.

We should note that other growth parameters like gas flow and pressure also have significant effects on the growth behavior of ITO NWs. It was reported previously that vertically aligned ITO NWs grew on YSZ substrates at a temperature of 900 °C.^{89,97} The discrepancy in the growth temperature can be attributed to the fact that the gas flow and pressure in our experiment are much lower than the parameters used in previous reports. In control experiments, we increased the gas flow rate and/or pressure and could also get vertical ITO NWs. However, we did find that the control of the NW orientations was less reliable at high gas flow rate and pressure. As a result, we present only the growth results achieved with fixed gas environment here.

Figure 4-4. Growth time dependence for vertical nanowires. (a-e) SEM images of vertical ITO nanowires. The growth times are 5 min, 10 min, 20 min, 30 min, and 60 min, respectively. (f) Length of the nanowires as a function of growth time.

As shown in Figure 4-4, for the vertical NWs grown at 800 °C, the NW length linearly depends on the growth duration with a growth rate of about 8 nm/min. The SEM images reveal the growth process: first a buffer layer forms on the surface of

YSZ substrate, and the Au nanoparticles appear to be imbedded in the buffer layer with limited lateral mobility, which may facilitate the out-of-plane growth.

We further carried out extensive (S)TEM and reciprocal space mapping (RSM) experiments to investigate the crystalline structures of the planar, vertical and random NWs as well as their growth mechanism. Figure 4-5 is a HAADF-STEM (Z-contrast) cross-section image of a planar NW. To prepare this type of cross-sectional samples, we applied the focused ion beam (FIB) lift-out technique. The bright-contrast Au catalyst particle can be identified at the top of the NW. As an important clue to the growth mechanism, we note that there is no buffer layer between the ITO NW and the YSZ substrate. In Figure 4-5b, a selected area ED (SAED) pattern taken near the Au/ITO interface suggests the following epitaxial relationships: $\text{ITO}_{[010]} // \text{Au}_{[-111]}$ and $\text{ITO}_{[001]} // \text{Au}_{[211]}$. Our TEM observations on several samples suggest that the NWs strictly grow along $[010]$ and $[001]$ directions, which explains the four-fold symmetry observed in SEM experiments.

Figure 4-5. Structural characterization of planar ITO NWs. (a) Low-magnification HAADF-STEM image of planar ITO NWs on a (100) YSZ substrate. Scale bar, 50 nm. (b) SAED pattern taken from an area near the NW-catalyst interface. (c) Geometrical phase analysis data taken along the [100] and [010] directions of YSZ. (d) High-resolution ADF-STEM image of the cross-section of an ITO NW. Scale bar, 5 nm. (e) High-resolution HAADF-STEM image of the tri-junction of the ITO NW, the YSZ substrate, and the Au catalyst particle. Scale bar, 10 nm. (f) ABF-STEM image of the interface between the ITO NW and the YSZ substrate. Scale bar, 1 nm. (g) Schematic illustration of the growth process of the planar ITO NWs.

Geometrical phase analysis (GPA) was applied to the acquired HRTEM images to

investigate the deformation and strain state of the planar ITO NWs. The uniform color shown in Figure 4-5c indicates little deformation of ITO NW, and the small strain is homogeneously distributed. Figure 4-5d is a cross-section ADF-STEM image of a planar NW, showing the expected rectangular shape with slightly faceted corners. Furthermore, the strong diffraction contrast right at the interface of ITO and YSZ, together with the presence of misfit dislocations at the interface (black arrows) indicates heightened strain at the interface, but the lattice is almost fully relaxed inside the NW. In Figure 4-5e, a HAADF-STEM image taken at the ITO/YSZ/Au tri-junction confirms the good epitaxial relationship between the ITO NW and the YSZ substrate. The ABF-STEM image in Figure 4-5f further reveals the excellent matched lattices at the ITO/YSZ interface. These observations shed light on the growth mechanism, and the process of growing planar NWs is illustrated in Figure 4-5g. At 900 °C, the absorption and desorption of precursor atoms are balanced on the bare YSZ surface, leading to no ITO film growth. However, as soon as the temperature lowers, the Au nanoparticles are effective in absorbing and retaining the precursor atoms for the subsequent ITO NW growth. In addition, the excellent lattice match between ITO and YSZ means that the interface energy is small, facilitating the in-plane growth.

Figure 4-6. Characterization and growth mechanism of vertical ITO NWs. (a) Cross-sectional HAADF-STEM image of the out-of-plane ITO NWs. Scale bar, 100 nm. (b) High magnification HAADF-STEM image for the marked rectangular area in (a). Scale bar, 50 nm. (c) HAADF-STEM of the interface (marked by yellow arrows) between the ITO NW and the YSZ substrate. Scale bar, 5 nm. (d) Schematic illustration of the growth process of vertical ITO NWs, concurrent with the formation of a buffer layer.

In stark contrast to the in-plane case, the HAADF-STEM images in Figure 4-6a and 4-6b reveal vertical out-of-plane NW growth and the existence of an ITO buffer layer with a thickness of about 40 nm. In Figure 4-6c, the high resolution HAADF-STEM image taken at the interface between an ITO NW and the YSZ substrate confirms the good epitaxial relationship between both. The buffer layer probably restricts the lateral movement of the Au catalyst nanoparticles on the bare YSZ surface, promoting the out-of-plane NW growth. As illustrated in the schematic in Figure 4-6d, the existence of such a buffer layer may be the critical factor triggering the out-of-plane

growth of ITO NWs.

Figure 4-7. TEM images of SnO₂ nanowires. (a) Low-magnification TEM image of the randomly oriented nanowires. Scale bar, 200 nm. (b-c) High magnification images of nanowires with a zigzag shape, shown in the red rectangular area A in (a). Scale bar, 50 nm in (b) and 10 nm in (c). (d) TEM image of the nanowire shown in the rectangular area B in (a). The nanowire shows a twinned structure. Scale bar, 50 nm. More details can be found in the HRTEM image in (e). The inset SAED pattern confirms the twinning. Scale bar, 10nm.

The randomly oriented NWs clearly possess a more complicated and less

controllable structure. Apart from the normal SnO_2 NWs with smooth surfaces, two unusual zigzag and twin structures are also present in Figure 4-7. We attribute their formation to the low growth temperature. One reason is that more tin vapor will be generated than indium vapor at low temperature, which will change the normal ratio of In/Sn. The other reason is that defects are more easily formed at low temperature because of the lower mobility of the constituting atoms.

Figure 4-8. Reciprocal space maps of planar and vertical ITO NWs. (a-b) (002) HL and (-204) HL reciprocal space mapping data of the planar ITO NWs grown on the (100) YSZ substrate. (c) Schematic illustration of the deformed orthorhombic ITO unit cell on the cubic YSZ. (d-e) (002) HL and (-204) HL reciprocal space mapping data of the vertical ITO NWs grown on the (100) YSZ substrate. (f) Schematic illustration of the cubic structured ITO unit cell on the cubic YSZ substrate.

As shown in Figure 4-8, we further used the synchrotron-based RSM technique to precisely measure the crystalline structure and the strain state of the ITO NWs. Figure

4-8a shows the mapping data of the planar NWs near the (002) diffraction spot of the YSZ substrate, and the identical H value of the ITO ($L \sim 2.0380$) and YSZ ($L \sim 1.9998$) peaks indicate excellent alignment at the interface without any inclination. In Figure 4-8b, the mapping data obtained near the (-204) diffraction spot reveal two ITO peaks with almost equal intensity. They can be attributed to the diffraction of two groups of planar NWs perpendicular to each other. Furthermore, the identical L value of both peaks indicates the same vertical lattice constant, whereas the different H values suggest difference in lateral lattice dimensions. We calculated the lattice constants of the planar ITO NWs as: $a = 10.118(5) \text{ \AA}$, $b = 10.192(5) \text{ \AA}$, and $c = 10.107(2) \text{ \AA}$, which suggests an orthorhombic distortion of the ITO cubic structure. Comparing with the lattice constants of the bulk ITO materials (cubic bixbyite structure, $a = 10.138 \text{ \AA}$), we can conclude that a and c axes of the planar NWs are slightly compressed while b axis is elongated. The schematic in Figure 4-8c illustrates the two equivalent deformation cases of ITO unit cells on the YSZ substrate, and the anisotropy of in-plane lattice parameters is apparently related to the NW growth. It is remarkable that the strain in the planar ITO NWs is anisotropic and smaller than 0.5%, even though the lattice mismatch between ITO and YSZ bulks is much larger at 1.6%, indicating effective stress relief in NWs.

Similarly, for the vertical NWs, the mapping data in Figure 4-8d at the (002) diffraction spot indicates no inclination between the NWs and the substrate. However, different from the in-plane case, the single (-204) peak for ITO in Figure 4-8e indicates that the vertical ITO NWs have the same a and b values. The lattice

constants extracted from Figure 4-8d,e indicate that vertical ITO NWs are cubic structure with a constant of 10.138(2) Å. These results indicate that the mismatch strain is fully relaxed in the vertical NWs (Figure 4-8f), which differs from the case of planar NWs.

4.2.3 In-plane and out-of-plane ITO NWs grown on (110) and (111) substrates

The success of using growth temperature as the single parameter to tune the orientation of ITO NWs on (100) YSZ substrates encouraged us to extend the method to the growth on (110) and (111) YSZ substrates with varied crystallographic symmetries. The growth conditions were kept the same as those used in the growth on (100) YSZ substrates.

Figure 4-9a-b show SEM and TEM images of planar ITO NWs on a (110) YSZ substrate. The planar NWs exhibit four-fold symmetry, similar to the results obtained on (100) surface. However, careful SEM and TEM examinations revealed two types of cross-sectional shapes as shown in the inset of Figure 4-9a: The cross section of [001]-oriented NW is triangular, while that of [-110]-oriented NW is rectangular. Furthermore, the TEM data reveal that the two exposed facets of the triangular [001]-oriented NWs are (100) and (010) planes (Figure 4-10). Because the surface energy of (100) planes is lower than that of (110) planes,⁹⁸ the formation of (100) facets in NWs is favourable, leading to the triangular NW cross section. On the other hand, the cross section of [-110]-oriented NWs is rectangular, which is similar to the cross section of NWs grown on (100) substrate. However, since the top plane of [-110]-oriented NWs

is (110), which has a higher surface energy than (100), the top plane of $[-110]$ -oriented NWs is not flat but split into small facets (Figure 4-10). The schematic diagram in Figure 4-9c summarizes the relationship between the ITO NWs and the (110) YSZ substrate.

Figure 4-9. Aligned ITO NWs on (110) and (111) YSZ substrates. (a,b) SEM images of planar ITO NWs on a (110) YSZ substrate at different magnifications. (c) Schematic illustration of planar ITO NWs on a (110) YSZ substrate. (d,e) SEM images of planar ITO NWs on (111) YSZ substrates at different magnifications. (f) Schematic illustration of planar ITO NWs on a (111) YSZ substrate. (g,h) SEM images of out-of-plane ITO NWs on a (110) YSZ substrate at different magnifications. (i) Schematic illustration of the out-of-plane ITO NWs on a (110) YSZ substrate. (j,k) SEM image of out-of-plane ITO NWs on a (111) YSZ substrate at different magnifications. (l) Schematic illustration of the out-of-plane ITO NWs on a (111) YSZ substrate. Scale bar, 1 μm in (a), (d), (g), (j); 100 nm in (b), (e), (h), (k); 20 nm in the insets of (a) and (d).

Following the same dynamic profile of growth temperature as shown in Figure 4-1a, we also successfully synthesized planar ITO NWs on (111) YSZ substrates. As shown in the SEM images in Figure 4-9d-e, the orientations of such NWs exhibit a three-fold symmetry. The cross-sectional TEM images of planar NWs on (111) YSZ are presented in Figure 4-10. The substrate orientation and the surface terminations of NWs are determined. As a general rule, planar NWs always grow along the projected orientations of their preferred growth directions on the substrate surface.^{21,99} It is well known that for ITO NWs the preferred growth direction is the [100] group.^{89,91,95,97} On the (111) plane, there are six equivalent projected directions of the [100] group: [1-21], [-12-1], [11-2], [-1-12], [-211], and [2-1-1]. However, because of the face-centered cubic crystal structure of YSZ, directions of [2-1-1], [-12-1], and [-1-12] are not equivalent to the other three. Remarkably, the observed three-fold symmetry of the NWs implies that the ITO NWs prefer to grow along only three of the six directions. This reliable selection of growth orientations appears to be a result of energetic minimization of ITO-YSZ interfaces, and it clearly warrants further investigation.

Furthermore, the width of the NWs shrinks along the growth direction, producing a “tie”-like morphology in the top view. Once again, we used the FIB sample preparation technique to cut the NWs and carried out cross-sectional TEM studies. Interestingly, as shown in Figure 4-11, the cross section of these NWs changes from a triangle to a trapezoid with increasing dimensions. The SAED pattern in Figure 4-11 reveals that the top surface of the trapezoid is (111), while the indexes of the side

walls are (1-13) and (13-1). We summarize the growth habit of planar ITO NWs on (111) YSZ substrate in Figure 4-9f.

With the same growth temperature profile shown in Figure 4-1d, aligned out-of-plane ITO NWs were grown on (110) and (111) YSZ substrates (Figure 4-9g-l). The good epitaxial relationship is similar to that in our previous report of ZnO NWs.¹⁰⁰ On the (110) YSZ substrate, there are two equivalent growth directions, i.e., [100] and [010], making an angle of 45° with the substrate surface (Figure 4-9i). These NWs are perpendicular to each other in the side view, but good alignment is achieved when projected on the (110) plane. While on the (111) YSZ substrate, there are three equivalent growth directions, i.e., [100], [010] and [001], and the NWs form an angle of 35.3° with the substrate surface (Figure 4-9l). Similar to the (110) case, these three oriented NWs are perpendicular to each other; on the other hand, as shown in the SEM image in Figure 4-9j, an angle of 120° is formed when the NWs are projected onto the (111) YSZ surface.

Figure 4-10. Cross-sectional TEM images of planar ITO nanowires grown on a (110) YSZ substrate. (a) Low-magnification TEM image of ITO nanowires taken in the [001] zone axis, revealing well defined triangular cross section. (b-c) HRTEM images collected in the area A in (a). The inset SAED pattern in (b) reveals the (100) surface termination. (d-e) Low magnification and HRTEM images of a planar nanowire taken in the [-110] zone axis. (f-g) ADF-STEM images of the nanowire.

Figure 4-11. TEM image of Planar nanowires on a (111) YSZ substrate. (a) SEM images of in-plane ITO nanowires on (111) YSZ surface. (b) Low-magnification ADF-STEM image of the cross section of the nanowires. (c-e) TEM (c) and HAADF-STEM (d-e) images, collected at positions 1, 5, and 4 in (b), respectively. (f) The SAED pattern of (e).

4.2.4 Planar ITO NWs grown with patterned catalyst

In order to better control the dimensions and positioning of the NWs, we patterned the Au catalyst into square arrays of dots using electron beam lithography (EBL). The

schematic of EBL patterning and NW growth processes is shown in Figure 4-12a. The diameter of the individual dots is 300 nm in Fig. 4-12b-c, 500 nm in Fig. 4-12d, and 400 nm in Fig. 4-12e while the thickness is kept at 20 nm. The separation distance between the dots in the square arrays is 4 μm . As shown in the SEM images in Figure 4-12b-d, planar NW arrays with expected symmetries were successfully obtained on (100), (110) and (111) YSZ substrates. One advantage of this scheme is that the growth directions of the NWs can be precisely determined by examining the final positions of the nanoparticles relative to the original patterns. We found that all NWs grew exactly from the periodic square positions of the Au dots defined by EBL, suggesting that the Au nanoparticles did not migrate before the start of NW growth. Furthermore, the regular Au catalyst dots lead to ITO NWs with uniform dimensions, and the morphology control is apparently superior to the method of initiating growth with nanoparticles produced in thermal ripening of Au thin films.

Figure 4-12. Regular arrays of planar ITO NWs. (a) Schematic illustration of site-specific planar ITO NWs grown from patterned Au catalyst nanoparticles. (b-d) (f-h) SEM image of the as-fabricated NWs with different magnifications on (100), (110) and (111) YSZ substrates, respectively. (e) (i) SEM image of NWs with different magnification, where the substrate with patterned catalyst was annealed at 900 $^{\circ}\text{C}$ for 1h. Scale bars: 5 μm in (b-i) and 1 μm in (f-i).

As shown in Figure 4-12b-d, for the growth results obtained on (100) and (110) YSZ substrates, we used four different colors to highlight the growth directions. Our SEM examinations of over a dozen locations confirm that the four in-plane orientations are statistically equivalent. Similarly, we labeled the NWs grown on (111) YSZ substrate using three different colors and found roughly equal populations of these NW groups along three growth directions. The table 4-1 provides details on the length and width of the NWs. As expected, the NWs grown along four equivalent directions on the (100) YSZ substrate exhibit identical length and width. Meanwhile, on the (110) YSZ substrate, the length of $[-110]$ -oriented NWs with rectangular cross section ($1.76 \pm 0.31 \mu\text{m}$) is notably larger than that of the $[001]$ -oriented NWs with triangular cross section ($1.36 \pm 0.29 \mu\text{m}$). The difference in length can also be seen in the high-magnification SEM images, which indicates that the NW growth speed is higher along $[-110]$ than that along $[001]$. Finally, the NWs on the (111) YSZ substrate show uniform tie-like morphology, consistent with the fact that the three growth directions are equivalent. As a note on the side, uniform dispersed Au nanoparticles with controlled density can also be achieved by using polymer encapsulation that provides tailored electrostatic repulsion in a solution environment.¹⁰¹ The use of this bottom-up strategy in future research will enable the scale up synthesis of ITO NWs with controlled morphologies.

Table 4-1. The length and width of in-plane nanowires on (100), (110) and (111) YSZ substrates, respectively, using patterned gold catalyst.

(100) YSZ	Length (μm)	Width (nm)
Yellow (moving left)	1.12 ± 0.12	305 ± 39
Red (moving right)	1.22 ± 0.16	289 ± 35
Blue (moving down)	1.18 ± 0.09	297 ± 39
Green (moving up)	1.16 ± 0.13	306 ± 39
(110) YSZ	Length (μm)	Width (nm)
Yellow (moving left)	1.71 ± 0.28	291 ± 48
Red (moving right)	1.81 ± 0.34	303 ± 34
Blue (moving down)	1.42 ± 0.24	271 ± 28
Green (moving up)	1.30 ± 0.35	299 ± 41
(111) YSZ	Length (μm)	Width (nm)
Red (moving left)	1.75 ± 0.08	543 ± 46
Yellow (moving right-up)	1.71 ± 0.08	529 ± 52
Blue (moving right-down)	1.72 ± 0.09	528 ± 67

The fact that the orientation of ITO NWs on YSZ substrates, i.e., planar, vertical or random, can be reliably realized by solely tailoring the growth temperature profile indicates the dominant role of thermodynamics in the NW synthesis. The epitaxial relationship between the ITO NWs and the YSZ substrate is the key to exploring the rich growth behaviors of NWs on YSZ substrates with (100), (110) and (111) surfaces. The mismatch between ITO and YSZ is only 1.6%, smaller than the cases of ZnO on GaN (1.8%),⁷⁷ InAs on GaAs (7.2%),⁷⁶ GaN on sapphire (16%),⁷⁹ and GaN on SiC (3.4%).⁸¹ In the previous work on growing In_2O_3 nanowires on Si, the lattice mismatch is as large as 7%,⁷³ which compromises the synthesis of high-quality NWs. Conforming to the principles of energy minimization and interfacial epitaxy, ITO

NWs exhibit triangular, rectangular or trapezoidal cross sections, as well as a novel “tie”-like morphology with dimension modulation along the length of NWs. In terms of crystalline structure, little deformation and few defects were detected in our systematic TEM experiments, and the effect of strain due to lattice mismatch is locally confined at the ITO/YSZ interface. Our RSM results show that the cubic lattice of bulk ITO transforms to an orthorhombic one with slight anisotropy in the planar NWs, while the small lattice mismatch exerts no influence at all on out-of-plane vertical NWs. These features underscore the ITO/YSZ as one of the best systems available for investigating epitaxial growth of planar NWs.

On the thermodynamic aspect, Cao and Yang recently developed a theoretical model by introducing thermal fluctuation into the VLS process and concluded that higher growth temperatures tend to favor the growth of planar NWs.¹⁰² This is consistent with our observation: Regardless of the orientation of the YSZ substrate, the growth temperature of planar ITO NWs is always higher than that of the vertical and random ones. Recently, Zi and coworkers used a revised Gibbs-Thomson equation to rationalize the planar growth of InAs NWs.⁸³ By treating a planar NW as a semicylindrical structure, they proposed that planar NW growth is favored by smaller Au nanoparticles.⁸³ In fact, on the (100) YSZ surface, we also found that the average diameter of the planar ITO NWs (50 ± 9 nm) is much smaller than that of the vertical ones (140 ± 18 nm), revealing the important role of Gibbs-Thomson effect.

We should note that there are also kinetic factors at play in our experiments besides the conventional VLS mechanism: the time-dependent profile of growth temperature

as shown in Figure 4-1 must be properly controlled in order to precisely control the NW orientation. Particularly, in the growth of vertical NWs, the formation of ITO buffer layer is a concurrent process at the growth temperature of 800 °C and the confinement of catalyst nanoparticles dynamically guides the final orientation of NWs. Recently, in a study of planar ZnO NWs on sapphire, Nikoobakht and coworkers pointed out that the existence of ternary Au-ZnO-sapphire interfaces promotes the growth of horizontal growth.¹⁰³ On the other hand, no ITO buffer layer forms at the growth temperature of 900 °C, and planar ITO NWs grow as the temperature gradually cools to 800 °C. In our case, good wetting of Au on both ITO and YSZ surfaces appears to be prerequisite for the growth of planar ITO NWs. In a very recent theoretical study, using a continuum model for faceted NW evolution, Schwarz and Tersoff demonstrated that the in-plane “crawling” growth mode, among multiple distinct modes of steady-state growth, can exist in a wide stability range.⁸⁶ Experimentally, we found that subtle adjustments of substrate and catalyst conditions can lead to drastic changes in the growth products. For example, after we annealed the (110) YSZ substrate with patterned Au catalyst at 900 °C for one hour in air before the growth of NWs growth, the growth directions of ITO NWs decrease from four (Figure 4-12c and g) to two (Figure 4-12e and i). This refined preference of [-110]-oriented NWs with the rectangular cross section over [001]-oriented NWs with triangular cross section provides additional control on the growth orientation. Overall, the final growth morphology is the product of complex interplay of both thermodynamic factors like surface and interface energies and kinetic factors like

initial phase nucleation and growth history.

4.3 Summary

In summary, the unprecedented freedom of producing NWs with diverse morphologies, as highlighted by this work, open doors towards not only the fabrication of advanced nanostructure and devices based on orientation-controlled NWs but also better understanding on the rich mechanisms of NW growth. In this thesis, we limited our experiments to the morphology control of ITO NWs and the epitaxy-based growth mechanism; since ITO is the most widely used transparent conducting oxide, we expect that oriented ITO NWs will be used to a wide range of solar and light emitting nanodevices in future studies.

Chapter 5. Gibbs-Thomson Effect in the Growth of Planar Nanowires

5.1 Introduction

With the minimization of electronic devices, semiconductor NWs are considered as one of the most promising candidates as building blocks for next-generation nanodevices.⁴ Semiconductor NWs have been intensively studied for more than two decades,^{58,104} however, it is still quite challenging to precisely align and integrate as-fabricated free-standing NWs into planar architecture devices with high throughput. As discussed in chapter 4, though several approaches have been considered to assemble free-standing NWs into electronic devices,^{105,106} these approaches suffer from drawbacks like imperfect alignment, mechanical damage and solution contamination. Recently, the planar growth of semiconductor NWs catalyzed by patterned Au discs is reported as a novel concept which can integrate as-fabricated planar NWs into electronic devices without the need of alignment step and simplify the fabrication process.⁸⁰ Generally, large-scale self-assembled planar NWs with controllable size and growth directions are grown epitaxially on substrates which are the same materials or low-mismatch crystal.^{75,77,79,107,108} Although several reports have discussed the fabrication of planar NWs, the study of their growth mechanism, particularly the famous Gibbs-Thomson effect, is still limited.

Gibbs-Thomson (G-T) effect is a universal physical phenomenon which describes the chemical potential difference across a curved surface. In the growth of semiconductor NWs, G-T effect was observed very often. Four decades ago,

Givargizov reported G-T effect in the VLS growth of Si NWs and verified a quadric order dependence of growth velocity on supersaturation.⁵³ Afterwards, lots of groups have reported G-T effect in different kinds of free-standing NWs *via* vapor-phase or solution-phase growth approaches.^{54,55,109-115} For example, Dayeh and Picraux reported a direct observation of G-T effect in Ge semiconductor NWs through a chemical vapor deposition (CVD) method;⁵⁴ Lee and co-authors demonstrated G-T effect on ZnO NWs through a solution-based growth approach.⁵⁶ The direct consequence of G-T effect is the growth velocity of NWs is size-dependent: NWs with larger diameter are grown faster than the NWs with smaller diameter and the growth of NWs will cease when size of catalyst particle is smaller than the cutoff diameter. Although G-T effect has been widely observed and studied, till now, most studies are based on the growth of free-standing/vertical NWs and the study of G-T effect in planar NWs is limited. Because of the promising applications of planar NWs, studying G-T effect in the growth of planar NWs is becoming a significant topic. Recently, Zhang *et al* mentioned G-T effect on the lateral growth of GaAs NWs for the first time.¹¹⁴ But they didn't discuss the effect of cross section, surface energy and composition variation of NWs on G-T effect.

In this chapter, we systematically study G-T effect for the first time in planar ITO NWs grown on different oriented yttria-stabilized zirconia (YSZ) substrates with different compositions. Because of high transparency and conductivity, ITO NWs have been widely studied in LED, solar cells and transistors.^{92,93,96,97,116-118} In these previous reports, the orientations of ITO NWs are all free-standing. In chapter 4, we

reported a simple approach to grow ITO NWs laterally and found as-grown lateral NWs shown rich exposed surface facets including (100), (110), (111) and (113) on different oriented substrates.¹¹⁹ These exposed surfaces may modulate the free energy of ITO NW and affect G-T effect during the vapor transfer growth. Meanwhile our group has reported that tin concentration in ITO could be modulated from 1% to 6% by simply changing source compositions.⁹⁵ Therefore, ITO is a good platform to study G-T effect induced by compositions and surface energies of exposed facets. Here our systematic results show that growth behavior of lateral ITO NWs conforms to G-T effect in spite of the rich growth orientations, complicated morphologies and varied compositions, and the cutoff diameter and supersaturation are directly determined by exposed facets and compositions of NWs. In addition, we demonstrate that tin doping has great impact on NWs morphology. Our results bring insights into G-T effect in the VLS growth of planar NWs and inspire the study of guided growth of other semiconductor NWs.

5.2 Experiments and Results

5.2.1 Experimental procedures

The growth procedure of ITO/IO NWs in this chapter is very similar to that discussed in chapter 4. The differences are the growth pressure, growth time and source power composition. In order to facilitate the growth of small nanowires, we increased the growth pressure to 30 mbar and decreased the growth time to several minutes. The source power composition is a mixture of In_2O_3 , SnO_2 and graphite

powder with weight ratios of 0.6:0.4:1, 0.8:0.2:0.1, 0.9:0.1:1 and 1:0:1, respectively. After growth, in order to stop the growth as fast as possible, the Ar gas was shut down immediately and the quartz tube was taken out of the furnace and cooled down by fans.

The morphology of as-fabricated ITO/IO nanostructures was examined by field emission scanning electron microscopy (FESEM, JEOL JSM-6700F). Cross-sectional samples for TEM investigation were prepared using a focused ion beam (FIB, FEI Nova 600). High-resolution TEM (HRTEM) imaging and electron diffraction (ED) were carried out on a FEI Tecnai F30 transmission electron microscope.

5.2.2 ITO Nanowires grown on (100), (110) and (111) substrates

In order to modulate the size of ITO NWs systematically, we used patterned gold discs with size from 60 nm to 870 nm defined by Electron-beam lithography (EBL) as catalyst. The pitch between two adjacent discs is set as long as 10 μm so that the synergetic effect is eliminated.¹²⁰ The source power is composed of $\text{In}_2\text{O}_3\text{:SnO}_2\text{:C}$ with a weight ratio of 0.6:0.4:1.

Figure 5-1 shows representative scanning electron microscope (SEM) images of as-fabricated ITO NWs on (100), (110) and (111) YSZ substrates, respectively. The morphology and growth directions of ITO NWs are similar to the results in chapter 4. As shown in Figure 5-1a, the NW grown on (100) substrate have a rectangular cross section and show a 4-fold symmetry from top view. The length of NWs increases with increasing catalyst nanoparticles showing a size-dependent growth velocity. Figure 5-

1b-c show the representative morphologies of ITO NW grown on (110) substrate. The [110]-oriented NW has rectangular cross section, therefore we name it (110)-R NW. The [100]-oriented NW has triangular cross section, and then we name it (110)-T NW. Because of their different cross sections, the length of (110)-R and (110)-T NWs are examined separately. In spite of their different morphologies, the length of both (110)-R and (110)-T NWs increase with increasing catalyst nanoparticles showing a size-dependent growth velocity. As shown in Figure 5-1d, the cross section of ITO NW grown on (111) substrate is hexagonal which is more complicated than the former ones. Although the length of NWs shows a similar size-dependent growth velocity, the complex morphology makes their growth behaviors different from the former cases.

Figure 5-1. Morphology evolution of ITO NWs grown on different oriented YSZ substrates. (a) SEM images of ITO NWs on (100) substrate. (b,c) SEM images of [110]- and [100]-oriented ITO NWs on (110) substrate, respectively. (d) SEM images of ITO NWs on (111) substrate. The insets in (a-d) show the corresponding cross-sectional TEM images of NWs. Scale bar: 1 μm for (a-d) and 20 nm for the insets in (a-d).

In ITO NW, tin doping concentration not only has great influence on its optical and electronic properties^{95,121} but also can change its surface energy. In this chapter, in order to study the influence of surface energy on G-T effect, we modulate the tin doping concentration intentionally by reducing SnO₂ ratio in the source power. We use another two different types of source power with composition as In₂O₃:SnO₂:C=0.8:0.2:1 (wt%) and In₂O₃:SnO₂:C=0.9:0.1:1, (wt%) respectively. As shown in Figure 5-2a-c, the length of NWs grown on (100) and (110) substrate show the size-dependent growth velocity (G-T effect).

Due to G-T effect, the supersaturation in NWs, which is the driving force for NWs growth, is size-dependent as described by the G-T equation.¹²²

$$\Delta\mu = \Delta\mu_0 - \frac{4\Omega\alpha_{vs}}{d} \quad (1)$$

where $\Delta\mu_0$, Ω , d and α_{vs} denote the supersaturation between vapor and solid with infinite radius of curvature, the atomic volume of the growth species, the diameter of the liquid droplet, and the average surface energy, respectively. Many papers reported that the growth velocity has quadratic dependence on saturation if the surface diffusion is negligible,¹²³⁻¹³¹ the scenario which is applicable for ITO NWs growth. The NW average growth velocity ($v = l/t$) has a quadratic relationship with the supersaturation, $v = b(\Delta\mu/kT)^2$, where b is a kinetic coefficient of crystallization, k is Boltzmann's constant, and T is temperature. As a result, equation 1 can be re-written as

$$\sqrt{v} = \sqrt{b} \frac{\Delta\mu_0}{kT} - \sqrt{b} \frac{4\Omega\alpha_{vs}}{kT} \frac{1}{d} \quad (2)$$

According to this equation, the square root of the growth velocity has a linear relationship with the reciprocal of the catalyst particle diameter. If we set $v=0$, we get so-called cutoff diameter:

$$d_c = \frac{4\Omega}{\Delta\mu_0} \alpha_{vs} \quad (3)$$

It means the NWs growth will cease when the size of catalyst particle is smaller than the cutoff diameter.

Figure 5-2. Length and growth velocity of ITO NWs grown on different oriented substrates illustrating the Gibbs-Thomson effect. (a-c) Length of NWs grown on (100) and (110) substrate as a function of catalyst diameter. **(d-f)** Square root of growth velocity of NWs grown on (100) and (110) substrate as a function of the reciprocal of the catalyst diameter. In **(a-f)**, the different colors indicate the different tin concentrations in the source. The weight ratios of $\text{In}_2\text{O}_3/\text{SnO}_2/\text{C}$ are 0.6:0.4:1 for red color, 0.8:0.2:1 for green color and 0.9:0.1:1 for blue color.

The equation (1)-(3) are general forms of G-T effect derived from the model of vertical cylinder NWs. But, in our case, NWs are grown laterally and the cross section is not round, so G-T equation has a different form. In the discussion part, we show that G-T equations for as-fabricated planar NWs have the same dependence as equation (1)-(3), so equation (1)-(3) are still valid for our case. We fit the plot of length of NWs against catalyst size with a quadratic function in Figure 5-2a-c which can clearly show the increasing cutoff diameter with decreasing tin doping concentration.

In Figure 5-2d-f, we plot the square root of growth velocity ($\sqrt{v}$) against the reciprocal of catalyst particle size ($1/d$) and fit data linearly according to equation (2). In spite of the different tin doping levels and morphologies, the growth behaviors of NWs grown on (100) and (110) substrates agree with G-T effect well. From these fittings, we can derive individual cutoff diameter for ITO NWs grown on different oriented substrate with different tin doping concentrations as listed in Table 5-1. The cutoff diameter decreases with increasing tin doping concentration which can be attributed to the surface energy variation. Normally, ITO has much lower surface energy than IO,¹³²⁻¹³⁶ so we speculate tin dopant may reduce surface energy. Therefore the cutoff diameter will decrease with increase tin doping level according to equation (3), $d_c = 4\Omega\alpha_{vs}/\Delta\mu_0$. The cutoff diameters of ITO NWs grown on different oriented substrate with the same composition will be discussed in elsewhere. It is worth to mention that the values in Table 5-1 are larger than what we obtained in chapter 4 (see Figure 5-3). This variation is due to the different growth recipes. In chapter 4, planar

ITO NWs are grown during the cooling down process from 900 °C to 800 °C. In this chapter, the growth temperature is kept stable at 850 °C. Because the cooling down process can increase the supersaturation $\Delta\mu_0$, which is analogous to the scenario of putting high temperature steam into a low temperature environment which can accelerate nucleation, a smaller cutoff diameter is expected according to equation (3), $d_c = 4\Omega\alpha_{vs}/\Delta\mu_0$.

Figure 5-3. Morphology and length statics of ITO NWs grown on (100) and (111) substrates. (a,b) SEM images of ITO NWs grown on (100) and (111) substrates, respectively. (c,d) The corresponding length statics for NWs in (a,b) as a function of catalyst diameter. (e,f) The square root of growth velocity of NWs in (a,b) as a function of reciprocal of catalyst diameter.

Table 5-1. Calculated Critical Diameters Based on Measured Results for ITO NWs.

Source Composition	100	110-R	110-T	111-W	111-R
(In ₂ O ₃ :SnO ₂ :C)	d _c (nm)	d _c (nm)	d _c (nm)	d _c (nm)	d _c (nm)
0.6:0.4:1 (wt%)	94	81	78	92	57
0.8:0.2:1 (wt%)	112	89	80	127	87
0.9:0.1:1 (wt%)	169	104	102	135	71

In contrast to the growth behaviors of ITO NWs on (100) and (110) substrates, ITO NWs grown on (111) substrate show an unprecedented growth scenario. In Figure 5-4a,b, the SEM images of ITO NWs grown on (111) substrate with less tin doping level are shown. The morphology of NWs has obvious difference from NWs catalyzed by small particle to NWs catalyzed by big particle. To be specific, for NWs catalyzed by small particle, the maximum width of NWs is much larger than the size of catalyst particle showing a rhombohedral shape (such rhombohedral shape is more obvious for lowest tin doping sample in Figure 5-4b). In contrast, for NWs catalyzed by big particle, the width of NW is close to the size of catalyst particle showing a normal wire shape. The forming mechanism of rhombohedral shape seems induced by the competition between axial and radical growth. We denote the rhombohedral NWs as (111)-R NWs and the wire-shaped NWs as (111)-W NWs. In Figure 5-4d-f, the lengths of ITO NWs with different tin doping level are shown. Unlike the cases in Figure 5-2a-c, the data cannot be fitted by a single function which means the growth behaviors of (111)-R and (111)-W are different. This trend is more obvious in the plot of $\sqrt{v}$ against $1/d$ as shown in Figure 5-4g-i. Therefore, the growth behavior of ITO NWs grown on (111) substrate can be divided into two separated regimes:

rhombohedral growth regime and wire-shaped growth regime. The data in Figure 5-4d-i is fitted by two corresponding functions instead of normal single function. From these fittings, the cutoff diameters are obtained which are listed in Table 5-1. One obvious trend is the cutoff diameter for (111)-W increase with decreasing tin doping concentration which is consistent with the cases on (100) and (111) substrates. The transition point from wire-shaped growth to rhombohedral-shaped growth increased slightly from 230 nm to 277 nm with decreasing tin doping level which means the tin dopant may promote the wire-shaped growth.

Figure 5-4. Morphology, length and growth velocity of ITO NWs grown on (111) substrates. (a,b) SEM images of NWs grown on (111) substrate. The weight ratios of In₂O₃/SnO₂/C in source are 0.8:0.2:1 and 0.9:0.1:1, respectively. Scale bars: 1 μm. (c) AFM image of NW grown with bigger catalyst. Scale bars: 1 μm. (d-f) Lengths of NWs grown on (111) substrate as a function of catalyst diameter with tin concentration of 0.4, 0.2 and 0.1 in source, respectively. (g-i) Growth velocities of NWs grown on (111) substrate as a function of reciprocal of catalyst diameter with tin concentration of 0.4, 0.2 and 0.1 in source, respectively.

In order to better understand the morphology of ITO NW grown on (111) substrate with the lowest tin doping level, we use atomic force microscopy (AFM) and transmission electron microscopy (TEM) to reveal its structure. As shown in Figure 5-4c, the AFM images show that the top surface of NW is flat and the sidewall of NW is rough and multi-faceted. Then we use TEM measurement and EDX mapping to observe the sidewall and the elements distribution. The lateral and axial cross-sectional samples are prepared by using focus ion beam (FIB) and in situ lift-out (INLO) techniques. The corresponding morphologies of lateral and axial cross sections are shown in Figure 5-5. In Figure 5-5a, the lateral cross section image shows that the thickness the NW is uniform which is consistent with AFM results. In the zoom-in image of the trijunction of catalyst, NW and substrate, we can see the interface between the catalyst and NW shows an inclined angle of 54° with respect to the substrate surface (Figure 5-5b). This interface can be easily identified as ITO (100) plane according to geometry relationship. In Figure 5-5C, the axial cross section image shows that the sidewall is composed of several high index facets. The fast Fourier transform (FFT) pattern and the interface image confirm the good epitaxial relationship between ITO NW and YSZ substrate with few defects (Figure 5-5d-f).

Figure 5-5. TEM characterization of low tin-doping ITO NWs grown on (111) substrate. (a) Low-magnification TEM image of lateral cross-section of NW. (b) Zoom-in image of the trijunction of NW, YSZ substrate and catalyst particle. (c) TEM image of axial cross-section of NW. (d) High-resolution TEM (HR-TEM) image of the interface between ITO NW and YSZ substrate. (e) Fast Fourier transform (FFT) pattern of the axial cross-section of NW. (f) Inverted FFT from ITO [211] and YSZ [211].

As shown in Figure 5-6, the EDX mapping shows that the tin dopants are distributed uniformly in both lateral and axial cross section. The gold catalyst can also be clearly distinguished.

Figure 5-6. The elemental analysis of axial and lateral cross section. (a) The morphology of axial cross section. (b,c) EDX mapping of axial cross section. (d) The morphology of lateral cross section. (e-g) EDX mapping of lateral cross section. The EDX mappings show that tin dopants are distributed uniformly.

5.2.3 Indium oxide (IO) nanostructures grown on (100), (110) and (111) substrates.

After successfully demonstrating the function of tin doping concentration on G-T effect in planar ITO NWs, we further study the growth of undoped indium oxide (IO) NWs. As shown in Figure 5-7, the undoped IO nanostructures grown on differently oriented substrate have quite different growth behaviors. In Figure 5-7a,b, pyramid islands, instead of NWs, are formed on (100) substrate. The schematic in Figure 5-7g illustrates the morphology of the pyramid island. The exposed facets are (111) plane that can minimize free energy because of the lowest surface energy of (111) plane in

IO. The (111) plane leads to the formation of [110]-oriented edge of island on (100) substrate. Our results are consistent with Egdell and co-workers' reports,¹³⁵⁻¹³⁹ they systematically studied the growth mechanism and structure properties of such pyramid islands on YSZ substrate. However, our results are different from their reports in two ways: (1) Our growth processes take place at a much higher pressure (30 mbar), while Egdell and co-authors use ultrahigh vacuum (10^{-5} mbar) for NWs growth; (2) We use Au discs as catalyst and the position where pyramid islands locates can be determined in advance, while Egdell and co-authors grow IO nanostructures *via* a vapor-solid (VS) process, where the NWs position cannot be controlled.

Figure 5-7. Morphology of indium oxide (IO) NWs grown on different oriented substrates. (a,b) (c,d) (e,f) are SEM images of IO NWs grown on (100), (110) and (111) substrates at different magnifications, respectively. Scale bar: 1 μm in (a,b) (d) (f) and 5 μm in (c) (e). (g-i) The corresponding schematics illustrating the morphology of IO nanostructures on (100), (110) and (111) substrates, respectively.

In Figure 5-7c,d, the morphology of IO NWs grown on (110) substrate are shown. One obvious feature is that [100]-oriented IO NWs are much longer than [110]-oriented IO NWs. After careful examination, we find the morphology of [110]-oriented IO NW is pyramided which is different from the ITO NWs ([110]-oriented ITO NWs have a rectangular cross section in Figure 5-1a). In order to minimize the surface energy, the exposed facets are prone to forming (111)-terminated planes which leads to the pyramid shape for [110]-oriented NWs. The morphology of [110]-oriented IO NW is also consistent with Egdell and co-workers' results.¹³⁶ Like the case on (100) substrate, our results are different from Egdell and co-workers' results in several aspects. Apart from the different growth pressure (30 mabr vs 10^{-5} mbar) and growth mechanisms (VLS vs VS) discussed in the last paragraph, the third aspect is we obtain both [110]- and [100]-oriented NWs while Egdell and co-workers only got [110]-oriented NWs. The reason is dictated to the growth mechanism (VLS vs VS). As shown in Figure 5-7h (the similar schematic can be found in Figure 5b of Egdell's paper), the exposed facets for [100]-oriented NWs are (100) planes while the exposed facets for [110]-oriented NWs are (111) planes. We know (111) planes have lower surface energy than (100) planes, so the nucleation energy barrier for growing [110]-oriented NWs is lower than [100]-oriented NWs. Therefore the growth of [110]-oriented NWs is favored. So in Egdell's reports, they obtained [110]-oriented NWs. But, in our experiments, we use VLS mechanism which can significantly decrease the

nucleation energy barrier for NWs growth. As a result, we can obtain both [110]- and [100]-oriented IO NWs.

In Figure 5-7e,f, the IO nanostructures grown on (111) substrate show rhombohedral islands. Interestingly, no NWs are formed on the surface. The orientations of these rhombohedral island point to one of the three equivalent [112] growth directions and show a 3-fold symmetry. The schematic in Figure 5-7i shows the corresponding morphology. The reason for the absent of IO NWs is due to the minimization of surface energy. As we discussed in our previous paper,¹¹⁹ NWs grown on (111) substrate would form (113) facets that have relatively high surface energy. Compared with IO surface energy, ITO has a lower surface energy so that ITO NWs can be grown but IO NW couldn't be grown on (111) substrate. In addition, IO nanostructure grown on (111) substrate is favor of forming (111) and (100) facet which result in rhombohedral architectures as illustrated in Figure 5-7i.

5.2.4 Discussion

G-T equation (1) is a general form for vertical cylindrical NWs. However, in our case, NWs are planar and their cross sections are not round. Both the surface energies of exposed facets and interface energy should be considered. Hence we develop a modified model to explain G-T effect for as-fabricated planar NWs.

Figure 5-8. Schematics illustrating the growth mechanism of ITO NWs on different oriented substrates. (a) The planar ITO NWs grown on (100) substrate. **(b)** The [110]-oriented NWs with rectangular cross-section grown on (110) substrate. **(c)** The [100]-oriented NWs with triangle cross-section grown on (110) substrate. **(d)** The wire-shaped nanostructure grown on (111) substrate. **(e)** The rhombohedral-shaped nanostructure grown on (111) substrate

As shown in Figure 5-8, the geometries of schematic in our models are based on TEM and SEM observations: both NW grown on (100) substrate and (110)-R NW have a rectangular cross section with a width-to-height ratio of about 2:1; (110)-T NW has a triangular cross section; (111)-W NW has a hexagonal cross section and (111)-R NW has a rhombohedral shape. G-T equations are derived from Gibbs free energies.⁸³ For given growth condition, Gibbs free energy changes (ΔG) during NWs growth can be expressed as:

$$\Delta G = \Delta N (-\Delta\mu_0) + \Delta S_{vs}\alpha_{vs} + \Delta S_{inter}\alpha_{inter} - \Delta S_{inter}\alpha_{ysz} \quad (4)$$

where ΔN denotes the atom number of growth species, $\Delta\mu_0$ is the supersaturation with infinite radius of curvature, ΔS_{vs} is the surface area increase, α_{vs} is the surface energy,

ΔS_{inter} is the interface area increase, α_{inter} is the interface energy, α_{ysz} is surface energy of YSZ. Hence, the supersaturation in planar NWs is given as:

$$\Delta\mu = -\frac{\Delta G}{\Delta N} \quad (5)$$

Based on the geometry in our models in Figure 5-8(a)-(e), we can derive the corresponding G-T equations for planar NWs, which are given as:

$$\Delta\mu_{100-R} = \Delta\mu_0 - \frac{\Omega}{d} (4\alpha_{vs,(100)} + 2\alpha_{inter,(100)} - 2\alpha_{ysz,(100)}) \quad (6a)$$

$$\Delta\mu_{110-R} = \Delta\mu_0 - \frac{\Omega}{d} (2\alpha_{vs,(100)} + 2\alpha_{vs,(110)} + 2\alpha_{inter,(110)} - 2\alpha_{ysz,(110)}) \quad (6b)$$

$$\Delta\mu_{110-T} = \Delta\mu_0 - \frac{\Omega}{d} (4\sqrt{2}\alpha_{vs,(100)} + 4\alpha_{inter,(110)} - 4\alpha_{ysz,(110)}) \quad (6c)$$

$$\Delta\mu_{111-W} = \Delta\mu_0 - \frac{\Omega}{d} \left(\frac{16}{3\sqrt{3}}\alpha_{vs,(113)} + \frac{4}{3\sqrt{3}}\alpha_{vs,(111)} + \frac{4}{3\sqrt{3}}\alpha_{inter,(111)} - \frac{4}{3\sqrt{3}}\alpha_{ysz,(111)} \right) \quad (6d)$$

$$\Delta\mu_{111-R} = \Delta\mu_0 - \frac{\Omega}{d} (2\alpha_{vs,(111)} + 2\alpha_{inter,(111)} - 2\alpha_{ysz,(111)}) \quad (6e)$$

The G-T equations (6a)-(6e) have the same structures, so they can be re-written as:

$$\Delta\mu = \Delta\mu_0 - \frac{\Omega}{d} \alpha_{effective} \quad (6)$$

where Ω denotes the atomic volume, d is the diameter of the catalyst nanoparticle and $\alpha_{effective}$ is the effective surface energy. If we assume $\Delta\mu = 0$, we obtain the cutoff diameter for planar NWs:

$$d_{c,p} = \frac{\Omega}{\Delta\mu_0} \alpha_{effective} \quad (7)$$

The equation (6) and (7) has the same dependence as equation (1) and (3) so the analysis based on equation (1) and (3) is still valid. The derivation procedure for equation (6a)-(6e) is available in Appendix 1. The $\alpha_{effective}$ is related to the geometry of NWs which can be used to explain the different cutoff diameters of ITO NWs grown on different oriented substrate under the same growth conditions.

Because of the complicated geometry and varied composition of NWs, for the growth models in Figure 5-8, we don't know the exact value of $\alpha_{effective}$ for every growth model under specific growth recipe. Here we just analyze them qualitatively based on their geometry.

Usually, the exposed surface can be considered as a type of crystal defects because of the dangling chemical bond and the surface energy is larger than the interface energy if the interface stress is not obvious. We know the crystal mismatch between ITO NW and YSZ substrate is $\sim 1.6\%$ ⁸⁹⁻⁹¹ and the lattice distortion of ITO NW is $\sim 0.5\%$.¹¹⁹ So the interface stress is minimal in our case. As a result, the surface energy contributes the majority of effective surface energy, $\alpha_{effective}$. For NWs grown on (110) substrate, (110)-R NW has three exposed facets while (110)-T NW has two exposed facets. So (110)-R NWs will have higher effective surface energy compared with (110)-T NWs. According to equation (7), (110)-R NWs will have bigger cutoff diameter compared with (110)-T NWs, which is consistent with experimental observations. Similarly, for NWs grown on (111) substrate, (111)-W NWs have 5 exposed facets and 4 of them are high index planes. Meanwhile (111)-R NWs have 3 exposed facets and the majority of facets area, the top facet, is low energy plane (111). So (111)-W NW has higher effective surface energy which leads to bigger cutoff diameter. This conclusion is also consistent with experimental observations. If we compare (110)-R and (100)-R NWs, their sidewalls are both (100) facets. The effective surface energy is determined by the top facet. In Zhang's paper, he reported that the surface energy of (100) facet is larger than that of (110) facet in In_2O_3 by first-

principle calculation.¹³⁶ This trend may be also true in ITO so that (100)-R will have higher effective surface energy than (110)-R NW because of higher (100) surface energy which results in bigger cutoff diameter. For (111)-R structure, the majority facet is (111) which is the lowest energy surface. So (111)-R structure has the lowest effective surface energy and lowest cutoff diameter in our models. This is consistent with experimental results.

5.3 Summary*

In conclusion, we systematically study G-T effect in the growth of planar ITO NWs on (100), (110) and (111) substrate, respectively. Our results show that G-T effect can be modulated by both substrate orientation and tin doping concentration. A growth model based on surface energy is developed to explain the observing increasing cutoff diameter with decreasing tin doping concentration and the lowest cutoff diameter for (111)-R NWs Growth. Overall, our report is the first comprehensive study of G-T effect on planar NWs and fills the research gap which will advance the research of planar NWs and inspire the study of G-T effect on other materials.

*Note: This work is going to be submitted to Nature Communications.

Chapter 6. Synthesis of Nanocone-Nanowire Kinked Nanostructures

6.1 Introduction

For the past two decades, semiconductor nanowires (NWs) have been intensively studied because of their wide applications in electronics, photonics, chemical/biological sensing, and energy harvesting/conversion technologies.^{58,104} The rational design and control of the growth dynamics and the NW architecture is of tremendous interest.⁴ So far, some novel structures, such as superlattice NWs,³⁴ heterostructures,^{18,140} in-plane NWs,⁸⁰ branched structures,^{39,45,97,141} kinked NWs,⁴³ nanosprings⁴¹ and nanowebs,⁴² have been reported. Among them, kinked structures not only bring new understandings to the growth mechanism but also promise potential applications. For example, Lieber and co-workers demonstrated the fabrication of U- and V-shaped kinked Si NWs and applied such kinked NWs as a probe to monitor three-dimensional intracellular signals in biological systems.¹⁴²⁻¹⁴⁴ Ma and co-authors reported the construction of near-infrared photodetectors based on kinked GaSb/GaInSb heterojunctions.¹⁴⁵

Several approaches have been exploited to switch the NW growth directions by modulating the growth conditions, i.e., growth pressure,²² reactant concentration,²⁹ growth temperature,³⁸ reactant species,^{146,147} and NWs surface passivation.^{148,149} The general principle is to change the contact angle between the liquid droplet and the solid NW by modulating the supersaturation in the liquid catalyst, and the resultant change of growth direction leads to the formation of kinked nanostructures. However,

the abrupt modulation of growth conditions may bring structural defects like twin boundaries and stacking faults into the nanostructures.^{24,37,44,146,147,150,151} Though the approach of NWs surface passivation could avoid bringing structural defects,^{148,149} it may cause chemical contamination. Therefore, it is significant to develop a new approach for the fabrication of kinked nanostructures. Meanwhile, so far, most kinked nanostructures are based on IV (Si and Ge) and III-V (InP, GaP and GaAs) semiconductors. It remains as an open question whether kinked NWs can be synthesized for other materials systems, and particularly, there has been no report on the kinked nanostructures of metal oxides yet.

Metal oxide NWs are promising building blocks for electronic devices owing to their wide bandgap, excellent optical and electrical properties, high stability in oxidizing environment, high crystalline nature and low-cost fabrication.¹⁵² Among them, In₂O₃ is an important metal oxide semiconductor with important applications in UV detector, gas sensors and transparent transistors.^{116,153-163} However, so far, there has been no report on controlling the growth behavior of In₂O₃ NWs.

In this chapter, we demonstrate the switching of growth directions and the formation of the nanocone-nanowire (NC-NW) kinked nanostructures of In₂O₃. Different from the previous reports, our synthesis does not entail any abrupt modulation of growth conditions, and as a result the kinked structures are free of structural defects and chemical contaminations. In addition, our systematic experiments revealed strong correlations between the rich morphologies of In₂O₃ nanostructures and the growth conditions during the vapor transport growth. The

switching of the growth orientations appears to be induced by the size-dependent free energies of the Au catalyst nanoparticles. Our results advance the vapor-liquid-solid (VLS) growth of novel nanostructures and the approach may be generalized to other functional materials.

6.2 Experiments and Results

6.2.1 Experimental procedures

The growth procedure of typical mixed type-I and type-II NC-NW kinked In_2O_3 nanostructures is similar to the growth procedure of ITO NWs discussed in Chapter 4. The differences are the growth parameters like source composition, growth pressure and growth time. A mixture of In_2O_3 and graphite powder with weight ratio of 1:1 was used as the source. The pressure inside the tube was fixed at 1 mbar during the growth process. The furnace was heated up to 800 °C at the fixed heating rate of 50 °C /minute. The growth time is as long as 10 hours. After growth, the furnace was cooled down naturally.

The morphology of as-fabricated In_2O_3 nanostructures was examined by field emission scanning electron microscopy (FESEM, JEOL JSM-6700F). The conventional θ -2 θ XRD investigation was done in an x-ray diffractometer (Bruker D8, $\lambda=1.54184$ Å). The high-resolution TEM (HRTEM) was carried out on a FEI Tecnai G2 30 UT transmission electron microscope operated at 300kV. The tomographic reconstructions were taken in HAADF-STEM mode on a JEOL 3000F TEM/STEM microscope operated at 300kV. Reconstruction was performed using 50 iterations

within the SIRT reconstruction algorithm supplied in FEI inspect 3D software.

6.2.2 Mixed type I and type II nanocone-nanowire kinked nanostructures

Figure 6-1 shows the morphology of a typical kinked In_2O_3 nanostructure. The vertical nanocone (NC) bases and the kinked NW tips can be clearly seen in Figure 6-1a. The angle selective backscattered (ASB) SEM image in Figure 6-1b reveals the catalyst nanoparticles at the apex of NWs, which confirm the dominant role of VLS mechanism in the NWs growth. However, the tapered morphology of NCs indicates that the contribution of vapor-solid (VS) growth mechanism cannot be totally excluded. Furthermore, as shown in Figure 6-1c, the NW tips form an angle of either 118° or 145° with respect to the NC bases, indicating that the kinked architectures consist of two different types. Extensive top-view SEM images were collected, and typical examples are shown in Figure 6-1d,e. At the first glimpse, the NW tips seem to exhibit random orientations. But careful examinations revealed that these NWs could be divided into two types. For the type-I NWs, the NW tips point to three equivalent directions, following the three-fold symmetry of the [111] yttria-stabilized zirconia (YSZ) substrates. On the other hand, for the type-II NWs, there are small connection segments between the NC bases and the NW tips, and the NW tips exhibit six growth directions, forming an angle of $\sim 19^\circ$ with the type-I NW tips, as observed in the top view (Figure 6-1f).

Figure 6-1. (a) SEM image (tilting angle: 60°) of the kinked nanostructures. Scale bar: 2 μm . (b,c) Angle-selective backscattered (ASB) SEM images of the kinked nanostructure at different magnifications (tilting angle: 60°). Scale bars: 1 μm in (b) and 500 nm in (c). (d,e) SEM top-view images of the kinked nanostructure at different magnifications. Scale bars: 1 μm in (d) and 500 nm in (e). The false colors denote the corresponding orientations of NW segments as shown in the schematic illustration in (f).

In order to better understand the differences of these two types of NC-NW kinked nanostructures, X-ray diffractometry (XRD) and High-resolution transmission electron microscopy (HRTEM) were used to investigate their crystalline structures. As shown in Figure 6-2, the XRD pattern shows that in spite of the structural complexity of the kinked nanostructures there is only a single and narrow In_2O_3 (111) diffraction peak with a full width at half maximum (FWHM) of only 0.17°. It indicates that the kinked nanostructures are single crystalline and the growth direction of the NC base is [111], confirming the good epitaxy relationship between the kinked

In_2O_3 nanostructures and the YSZ substrates. Such epitaxial growth is expected as a result of their matching lattice constants (In_2O_3 : 1.01170 nm; YSZ: 0.51423 nm).¹³⁶

Figure 6-2. XRD spectrum of as-fabricated nanocone-nanowire (NC-NW) kinked nanostructures.

The HRTEM results provide more details about the kinked nanostructures. During the TEM measurements, we found that it was often challenging to properly align the NCs and NWs to correctly determine their orientations. The complications come from the fact that the NC base is tapered with an angle of $\sim 10^\circ$ and the NW tips are often not positioned flat on the TEM grid. Because the type-I kinked nanostructure is structurally simpler, we take it as an example to explain the geometry of alignment. As shown in Figure 6-3, if the nanostructure is not properly aligned, the orientations of NCs and NWs shown in the selected area electron diffraction (SAED) patterns are not the correct growth directions.

Figure 6-3. (a) SEM image of a NC-NW kinked nanostructure on TEM grids. (b,c) Schematics illustrating the alignment complexity for the tapered sample during TEM characterization. (d,e) Real example showing the wrong growth directions we derived owe to misalignment.

As shown in Figures 6-4a1-a5, we used the “electron tomography” technique to yield a 3D reconstruction of the NC-NW kinked nanostructure based on a series of 2D projection images with a rotation interval of 2° . These 3D reconstruction images clearly show the difference between observed direction and real direction of NWs.

Figure 6-4. (a) Tomographic reconstruction of the type-I kinked nanostructures. Scale bar: 200 nm. (b,c) TEM images of the kinked nanostructure observed in $[001]$ and $[110]$ zone axes, respectively. Scale bars: 200 nm. (d,e) HRTEM images collected in the kinked region and the catalyst/NW interface. Scale bars: 10 nm in (d) and 5 nm in (e).

In a complementary geometric approach, we developed a procedure to use individual SAED patterns to determine the orientations of the NC and NW segments. First, we took two SAED patterns under two different zone axes. Although the growth directions of the NCs and NWs are unknown, the two planes which contain those directions can be identified based on the geometric relationships. Then, the growth direction for each segment can be derived because these two planes always intersect in a line as long as they are not parallel. In order to find the correct index of the intersecting line between two unparallel planes, we used the Wulff Net, which is a convenient and easy tool to measure angles between planes and to illustrate plane rotations.¹⁶⁴ In the Wulff Net, directions are represented as dots and planes are

represented as straight/curve lines. The advantage of Wulff Net is that it can clearly show the symmetry of a 3D structure in a 2D plot, simplifying the analysis. Here we use the derivation of the growth direction of NW tip as an example to illustrate our approach. As shown in Figure 6-4b,c, the two SEAD patterns taken under the zone axes of [001] and [110] indicate that the growth direction of the NW tip is the intersecting line of (010) and (1-11) planes. With the help of Wulff Net, we were able to derive that the correct growth direction of the NW tip is [110] (see Appendix 2 for more details). Due to the cubic symmetry of In_2O_3 , there are three equivalent [110] growth directions: [110], [011] and [101], which are consistent with the observed 3-fold symmetry in the SEM top-view images as shown in Figure 6-1d,e. In addition, we know the obtuse angle formed by [111] and [110] in a cubic lattice is about 145° , which agrees with the SEM observation in Figure 6-1c.

The HRTEM image in Figure 6-4d indicates that the kinked region of the In_2O_3 nanostructure is free of defects, which is different from the kinked nanostructures previously reported.^{24,37,44,146,147,150,151} In these previous reports, the defects including twinning planes or stacking faults were observed and believed to play an important role in promoting the formation of kinked structures. In Figure 6-4e, the HRTEM image collected at the interface between the catalyst nanoparticle and the NW tip shows that an ultrathin In_2O_3 shell covers the catalyst nanoparticle, which is similar to our previous observations on indium tin oxide (ITO) NWs.^{97,119}

Different from the type-I kinked nanostructures, the type-II kinked nanostructures are featured with a small connection segment between the NC base and the NW tip.

Nevertheless, by using the same geometric method, we were able to derive the growth directions for every segment by collecting SEAD patterns under different zone axes (Figure 6-5). The results show that the growth directions of NC base, connection segment and NW tip are $[111]$, $[110]$; and $[112]$, respectively (see Appendix 2 for more details). In order to testify the reliability of our approach, we chose another type-II kinked nanostructure and derived its growth directions using different zone axes. Because of the symmetry of cubic lattices, there are three equivalent $[110]$ growth directions: $[110]$, $[011]$ and $[101]$, and six equivalent $[112]$ growth directions: $[-112]$, $[-121]$, $[12-1]$, $[21-1]$, $[2-11]$ and $[1-12]$. In other words, there are three equivalent growth directions for the connection segments and six equivalent growth directions for the NW tips, which are consistent with the SEM observations (Figure 6-1d-f).

Figure 6-5. (a,b) TEM images of the type-II kinked nanostructure observed in $[110]$ and $[111]$ zone axes, respectively. Scale bar: 200 nm. (c) Tomographic reconstruction of the type II NC-NW kinked nanostructure. Scale bar: 200 nm. (d-f) HRTEM images collected in regions A, B and C as denoted in (a). Scale bars: 5 nm.

In fact, the same $[110]$ growth direction shared by the connection segment in the type-II nanostructure and the NW tips in the type-I nanostructure indicates the type-II nanostructure is actually a variant of the type-I nanostructure. As shown in Figure 6-1f, the six equivalent $[112]$ growth directions of the NW tips in the type-II nanostructures can be divided into three pairs, and each pair forms an angle of $\sim 19^\circ$ with one of the three $[110]$ directions with mirror symmetry. Moreover, we counted the numbers of the NW tips for both type-I and type-II kinked nanostructures based on their orientations (Figure 6-6). We examined several samples and the statistic results indicate that the counts for the three $[110]$ -oriented NW tips are roughly identical, which is also true for the six $[112]$ -oriented NW tips, which are consistent with their crystallographic equivalence in a cubic structure. The proportion for the $[110]$ -oriented NW tips switching their growth directions to $[112]$ ($\text{number}_{[112]}/(\text{number}_{[110]}+\text{number}_{[112]})$) is 28%~45%, slightly lower than 50%. In addition, the obtuse angel of 118° formed by $[111]$ and $[21-1]$ directions in a cubic structure agrees with the SEM observations in Figure 6-1c.

Figure 6-6. The SEM top-view images of as-fabricated NC-NW kinked nanostructures at low magnification and the corresponding statistics based on the NWs' orientation. The false color arrays indicate the different orientations. Scale bar: 1 μm .

In Figure 6-5a, the same SAED patterns collected in NC base, connection segment and NW tip confirm the single crystallinity of as-fabricated NC-NW kinked nanostructure. The HRTEM images in Figure 6-5d-f reveal that the kinked region is free of defects, which is also different from the kinked nanostructures reported previously.^{24,37,44,146,147,150,151} Similarly, we used the “electron tomography” technique to yield a 3D reconstruction for the type-II kinked nanostructure in Figure 6-5c.

In order to better observe their morphologies, the NC-NW kinked nanostructures were scratched from the substrate, transferred to a wafer, and examined by SEM. As shown Figure 6-7, the cross section of the NC base is hexagonal, which is a typical shape for [111]-oriented In_2O_3 NW.^{165,166} Both the type-I and type-II kinked nanostructures can be easily distinguished. In addition, we observe that the NC sidewall is not flat but consists of lots of tilted facets. The reason is the NC sidewall is favor of being split into lots of tiny (111)-terminated facets because of the lowest surface energy of In_2O_3 (111) plane.¹³⁶

Figure 6-7. (a-c) SEM images of the scratched NC-NW kinked structures. (d-i) The SEM images of the NC-NW kinked structure transferred to Si wafer. (e,f) are the zoom-in images in (a). In (h), these two types of structures can also be identified (see yellow arrays). In (h) and (i), the area indicated by red arrows show that the exposed surface of NC base consist of lots of tiny facets. Scale bar: 1 μm for (a-d) and (h), 100 nm for (e- f) and (h-i).

Moreover, we carry out time-dependent growth experiments to reveal the morphology evolutions from the NC to the NC-NW kinked nanostructure (Figure 6-8). During the growth of NC bases, the height and the size of the NC bases keep increasing while the diameter of catalyst nanoparticle keeps shrinking (Figure 6-9).

Figure 6-8. The time-dependent growth evolution of In_2O_3 NC-NW kinked structure grown on (111) YSZ substrate. (a-l) Top-view and tilted-view (30°) SEM images of as-fabricated structures with an growth time of 2h, 4h, 6h, 7h, 8h and 10h, respectively. The insets show the corresponding zoom-in images. Scale bar: 1 μm for (a-l), 200 nm for insets in (a-l).

Figure 6-9. Size statistics of NC-NW kinked nanostructures. (a) The diameter and height of NC as a function of growth time. (b) The diameter and length of NW tip as a function of the growth time.

The interesting observations from the SEM images are that the catalyst nanoparticle firstly moves to the NC sidewall and then advances the growth of NW tips (Figure 6-

10). Afterwards, the length and the size of NW tips increase continuously with growth time (Figure 6-8). Based on the time-dependent growth results, a clear picture about the growth sequences for the type-I and type-II kinked nanostructures can be drawn: [111]-oriented NC firstly switch its growth direction to [110] to form the type-I kinked nanostructure, and then less than a half [110]-oriented NWs switch their growth directions to [112] to form the type-II kinked nanostructure.

Figure 6-10. The morphology transition from NC to NC-NW kinked nanostructures. (a,b) SEM side-view images of NC grown at 800 °C for 6 hours with a growth pressure of 1 mbar. (c,d) SEM side-view images of NC-NW grown at 800 °C for 7 hours with a growth pressure of 1 mbar. Scale bars: 1 μm in (a-d) and 100 nm in the insets of (b) and (d).

In the transition from NC base to NW tip, the growth direction changed from [111] to [110]. Normally, the growth direction of NWs is correlated with the catalyst.²¹ One approach to manipulate the growth direction is to engineer the composition of catalyst

droplet during the VLS growth. For example: Wang *et al* reported that the growth direction of InP NWs could be switched reversible from [100] to [111] by varying the indium concentration in the catalyst droplet;²⁹ T. R. Kuykendall *et al* reported that they obtained [1-100]-oriented NWs by using gold-rich catalyst and [11-20]-oriented NWs by using nickel-rich catalyst;²⁸ Zhang *et al* reported that they obtained defect-free [00-1]-oriented Wurtzite InAs by using indium-rich catalyst and [000-1]-oriented Zinc-Blende InAs by using indium-poor catalyst.³⁰ However, in our experiments, the unchanged growth condition means the composition of catalyst droplet is stable, so the formation of kinked nanostructures are not induced by the catalyst engineering in our case.

On the other side, the growth direction of NWs is also correlated with the size of catalyst which has been reported as diameter-dependent growth direction by several groups: The smaller catalyst particle stimulates the growth of [110]-oriented NWs, while the bigger catalyst particle stimulates the growth of [111]-oriented NWs.²⁵⁻²⁷ Such size effect is due to the size-dependent free energy for different oriented NWs.²⁶ In our experiments, the size of the catalyst nanoparticle shrinks from ~200 nm to ~100 nm (Figure 6-11a). Therefore the switch of growth direction in our case seems due to the catalyst size effect. Meanwhile, the instability of catalyst nanoparticle at the NC apex is another important factor. Generally, the catalyst droplet might oscillate in the liquid/solid interface during the VLS growth and leads to the obvious features like periodic sidewall facets¹⁶⁷ and twining³⁴ in NWs. Schwartz and co-authors raised a kinetic model to explain the oscillation of catalyst droplet in the growth of Si NWs in

where they attribute the rich variety of morphologies to the crystal anisotropy,⁸⁴ and they further demonstrated the direct observation of the droplet jumping induced by mismatch between catalyst size and NWs diameter by using *in situ* TEM.¹⁶⁸ Moreover, the oscillation of catalyst droplet during the VLS growth of NWs have been directly observed in many other materials like Al₂O₃,⁸ Ge^{9,169} and GaP.¹⁷⁰ In our experiments, the Au catalyst particle may also oscillate at the NC apex which might be indirectly supported by the SEM observation of one-edge located catalyst at the NC apex (Figure 6-8c-f). When the catalyst size keeps shrinking during the growth, the smaller catalyst particle might be pinned to the sidewall and can't get unpinned. As a result, the pinned catalyst particle will catalyze the growth of NW tips (Figure 6-10).

Similar to Schmidt's paper,²⁶ we draw a plot of catalyst size-dependent free energy for different oriented NWs in Figure 6-11b. This schematic illustrates the switch of growth direction from [111] to [110] and [112] with decreasing catalyst particle size. In Wu's and Schmidt's reports, if the size of catalyst particle is in the middle range, both the [110]- and [112]-oriented NWs grow simultaneously,^{26,27} which means the free energies are very close between [110]-oriented NWs and [112]-oriented NWs. Such tiny differences of the free energy may also be true in our case so that some [110]-oriented NWs are able to change their growth directions to [112] direction caused by experimental fluctuation during the vapor transfer growth, leading to the formation of mixed type I and type II kinked structures.

Figure 6-11. (a) The diameter of catalyst nanoparticles as a function of the growth time with a growth temperature of 800 °C and a growth pressure of 1 mbar. (b) Schematic illustrating the free energy as a function of the catalyst diameter for [111]-, [110]- and [112]-oriented NWs with a growth temperature of 800 °C and a growth pressure of 1 mbar.

6.2.3 Temperature-and pressure-dependent growth

We demonstrate the rich growth behaviors of In_2O_3 NWs by systematically changing the growth parameters, i.e., the growth temperature and pressure. We use five growth temperatures, from 750 °C to 950 °C with a step of 50 °C, and two growth pressures: low growth pressure (1 mbar) and high growth pressure (30 mbar). The results are shown in Figure 6-12. Apart from the mixed type-I and type-II kinked nanostructures, three interesting results are highlighted in Figure 6-13. When the growth temperature is kept at 800 °C, the [110]-oriented NWs are grown directly on the substrate at high growth pressure (Figure 6-13a,b), which are similar to the previous reports.^{171,172} The reason why the growth direction of In_2O_3 NWs is favored in [111] direction at low growth pressure and in [110] direction at high growth pressure is not clear yet at this point. When the growth temperature is increased to 850 °C, both the type I NC-NW kinked nanostructures and [110]-oriented NWs are

grown (Figure 6-13c,d), which further confirms NWs are prone to growing in [110] direction at high growth pressure. When the growth temperature is further increased to 900 °C, vertical NWs terminated with (100) and (111) facets are formed at high growth pressure (Figure 6-13e,f). The disappearance of the catalyst particle is due to the high mobility and high solubility of gold in In₂O₃ NWs at high growth temperature, which agrees with previous reports.^{165,166,173}

Figure 6-12. The systematic study of temperature- and pressure-dependent morphology of In₂O₃ nanostructures. The growth pressure is 1 mbar and the growth time is 10h. Scar bar: 1 μm.

Figure 6-13. Temperature- and pressure-dependent growth behaviors of In_2O_3 nanostructures. (a,b) SEM top-view and tilted-view (20°) images of In_2O_3 NWs grown at 800°C with a growth pressure of 30 mbar. (c,d) SEM top-view and tilted-view (20°) images of the NC-NW kinked nanostructures grown at 850°C with a growth pressure of 30 mbar. (e,f) SEM top-view and tilted-view (20°) images of vertical In_2O_3 NWs grown at 900°C with a growth pressure of 30 mbar. (g,h) SEM top-view and tilted-view (20°) images of the uniform type-I NC-NW kinked nanostructures grown at 800°C with an increasing growth pressure from 1 mbar to 30 mbar during the growth of the NW tips. Scale bars: $1\ \mu\text{m}$ in (a-h); 200 nm in the insets.

6.2.4 Uniform type I nanocone-nanowire kinked nanostructures

Based on the temperature- and pressure-dependent control experiments, one

interesting result is the $[110]$ -oriented NWs are favorite and stable at high growth pressure. Therefore we slightly changed the growth recipe of mixed type-I and type-II kinked nanostructures by increasing the growth pressure from 1 mbar to 30 mbar during the growth of NW tips and obtained the uniform type-I NC-NW kinked nanostructures successfully (Figure 6-13g-h and Figure 6-14). These results confirm that the $[110]$ -oriented NW won't switch its growth direction to $[112]$ at high growth pressure. Similarly, we count the numbers of NW tips based on their orientations from the SEM top-view image and analyze their statistic. The statistic results indicate that the counts for the three $[110]$ -oriented NW tips are roughly identical, which are consistent with their crystallographic equivalence in a cubic structure.

Figure 6-14. (a) The SEM top-view image of as-fabricated uniform type-I NC-NW kinked nanostructures at low magnification. Scale bar: 1 μm . (b) The growth parameters for the uniform type-I kinked nanostructures. (c) The corresponding statistics of the NWs' orientations in (a).

We sum up the temperature- and pressure-dependent growth behaviors and use the schematic Figure 6-15 to show our result. Four representative nanostructures denoted as a-d are obtained successfully. The formation of these nanostructures is induced by

the growth dynamics and the crystal symmetry of In_2O_3 .

Figure 6-15. Schematics showing the rich growth behaviors of the novel In_2O_3 nanostructures under tailored growth conditions. (a-d) $[110]$ -oriented NWs, vertical NWs terminated with (100) and (110) , uniform type-I NC-NW kinked nanostructure c and mixed type I and type II NC-NW kinked structure are grown under specific growth conditions.

6.3 Summary*

In summary, the unprecedented rich growth behaviors for In_2O_3 NWs were demonstrated systematically by simply modulating the growth conditions in a conventional vapor transport growth method. Among the rich variety of nanostructures, a novel NC-NW kinked nanostructure induced by the catalyst size effect is highlighted. The type-I and type-II kinked nanostructures are identified and characterized carefully. Our results not only bring new insights in the growth

mechanism but also provide a convenient approach to fabricate kinked nanostructures that may have potential applications in the field of detectors and sensors.

*Note: This work is under review in Nano Letters.

Chapter 7. Conclusions and Outlook

7.1 Conclusions

In this thesis, we focused on the rational synthesis of tailored oxide semiconductor nanowires. Some novel nanostructures are obtained by modulating the growth parameters intentionally. The structural properties of as-fabricated nanowires have been studied by extensive TEM, SEM, XRD and AFM measurements. The main conclusions are as follows:

(1) We have successfully demonstrated the growth of laterally, vertically and randomly oriented nanowires by modulating the growth temperature. Our systematical results showed that the planar nanowire grown during the cooling down process and the buffer layer played a vital role to promote the growth of vertical nanowires. The formation of randomly oriented nanowires is due to the low reaction temperature of tin oxide and graphite and the mismatch between the tin oxide and YSZ substrate. The RSM results revealed the lattice relation in the nanowires. At last we also demonstrated the guided growth nanowires by using patterned catalyst.

(2) We have directly observed the Gibbs-Thomson effect in the growth of planar nanowires for the first time. Gibbs-Thomson effect is an important phenomenon which describes the chemical potential across a curved interface. In the growth of vertical nanowires, the Gibbs-Thomson effect is widely observed. However, the study of Gibbs-Thomson effect in planar nanowires is limited. In our research, we found the planar nanowires also conformed to the Gibbs-Thomson effect in spite of their complicated structures. Our results showed that the tin concentration and the exposed

surface had great effect on the Gibbs-Thomson effect and a growth model was developed to explain the different cutoff diameters.

(3) We have fabricated a novel nanocone-nanowire kinked nanostructure. Different from the previous growth methods, our growth method is much easier. We decreased the growth pressure and temperature intentionally to maintain the growth stability. We didn't need to change any growth condition and the kinked nanostructures formed naturally. Our study showed that the size-dependent growth direction was dictated to the formation of kinked nanostructures. Extensive TEM measurements revealed that as-fabricated kinked nanostructure was free of defects. Our control experiment showed that the growth of [110]-oriented nanowire was favored at high growth pressure and we successfully obtained the exclusive type I kinked nanostructure by slightly changing the normal growth recipe.

Overall, in this thesis we systematically study the VLS growth mechanism in In-Sn-O materials system. Our results bring new insights into the VLS growth mechanism and advance the research of semiconductor oxide nanowires.

7.2 Outlook

Semiconductor nanowires have been studied for more than two decades. In the first decade, researchers studied the fabrication of nanowires. In the second decade, scientists focused on the applications of semiconductor nanowires. A short review about the applications of semiconductor nanowires is given as follows.

7.2.1 Nanowire-Based Electronics

NWs are considered promising candidate for next-generation electronic devices because of their single crystalline nature and nanoscale size. NWs can be used as the channels in the field effect transistors (FETs) with cross-sectional size down to sub-100 nm². The advantages of NW-based FETs are the high performance and good compatibility with standard industry fabrication process.

Due to the high surface/volume ratio, NWs are very sensitive to the environment. NW-based chemical and light sensing devices have high sensitivity.¹⁷⁴ The working principle of such sensor is that the adsorbed materials will accept or donate electrons to the NW, modifying the conductance of NW. Till now, several kinds of NWs have been intensively studied as gas and biological sensors. The representative examples are the following. As shown in Figure 7-1, Kolmakov *et al* reported they used SnO₂ NW-based devices to detect O₂ and CO concentrations.¹⁷⁵ Their results showed that in a combustible gas environment (CO), the SnO₂ conductivity increased and in oxidizing environment (O₂), the SnO₂ conductivity decreased. This is because CO reacts with O and increases oxygen vacancy in SnO₂, so the carrier density increases. In contrast, O₂ depletes electrons from SnO₂ and forms a depleted region at the surface, so the carrier density decreases. Afterwards, several groups used the similar strategies to demonstrate the detection of humidity,¹⁷⁶ hydrogen¹⁷⁷ and NO₂¹⁷⁸ with SnO₂ NWs. Zhou *et al* reported the detection of NH₃ by using In₂O₃ NW-based sensor.¹⁷⁹ In another paper, they demonstrated the detection of NO₂ down to ppm level with In₂O₃ NW-based sensor, achieving the best record of NO₂ sensitivity.¹⁵⁴ A

similar phenomenon has been observed in ZnO ,¹⁸⁰⁻¹⁸³ and TiO_2 NW-based devices.^{184,185}

Figure 7-1. (a) Schematic illustrating the sensing mechanism of a SnO_2 NW-based sensor. A completely depleted, hence non-conductive state under an oxidizing ambient and sharply increased conductance due to electron transfer from a surface state back into the NW interior when a reducing gas is admitted. Taken from Ref. 175. (b) NW-based pH detector. Zoom of the aminopropyltriethoxysilane (APTES)-modified Si NW surface illustrating changes in the surface charge state with pH. Taken from Ref. 63. (c) Nanowire-based detection of single viruses. Specific binding of a single virus to the receptors on nanowire 2 produces a conductance changes. When the virus unbinds from the surface the conductance returns to the baseline value. Taken from Ref. 186.

The detection of biological materials by NW-based sensors is a very promising field, because the high sensitivity and fast response time enable the real-time measurement of biological materials.^{187,188} As early as 2001, Cui and co-authors for the first time demonstrated the detection of chemical and biological species using Si NWs.⁶³ Later on, they demonstrated the direct ultrasensitive measurement of DNA sequence by Si nanowire functionalized with PNA receptors.¹⁸⁹ Afterwards, many works demonstrated the real-time label-free detection of virus and cancer cells by decorating the NWs surface with proper molecules.^{62,186,190-193} As shown in Figure 7-a, the working principle is similar to NW-based gas detectors. The difference is that the biological materials do not react with nanowires directly, but through receptors bounded to the NW surface.

7.2.2 Nanowire-Based Photonics

NW-based waveguide: NWs are an excellent platform for optical waveguide applications because they are one-dimensional materials with high refractive index. Yang *et al* reported that a SnO₂ NW-based waveguide can effectively guide the propagation of 450-550 nm light with very low loss (1-8 dB/mm).¹⁹⁴ In another paper, they also demonstrated the direct photonic-plasmonic coupling between a O₂ NW and Ag NW.¹⁹⁵ Different from the homogenous NWs, Xu *et al* reported a composition gradient NW-based waveguide.¹⁹⁶ They used a CVD method to fabricate such unique composition gradient CdS_xSe_{1-x} NW and demonstrated symmetric light propagation phenomenon. These studies are useful to fabricate NW-based photonic circuits.

NW-based lasers: The first NW-based laser was demonstrated by Yang and co-authors in 2001.^{197,198} They used ZnO NW (~385) as gain medium. After that, many different NWs have been used to demonstrated as lasers, such as ZnS (~337 nm),^{199,200} CdS (~490 nm),²⁰¹⁻²⁰³ GaN (~375 nm)²⁰⁴⁻²⁰⁶ and GaSb (~1550 nm).²⁰⁷ In these lasers, high optical gain was obtained. The major limitation of NW lasers is the low reflectivity at the end facet of the NW. To solve this problem, Yang *et al* used nanorings as gain media.²⁰⁸ Furthermore, NWs made of various materials can be used to fabricate lasers. Fang *et al* demonstrated a multi-quantum-well NW based laser consisting of an InGaN shell and a GaN core.²⁰⁶ The wavelength could be engineered from 365 nm to 494 nm by modulating the quantum well structure.

NW-based plasmonics: Surface plasmons are collective oscillations of free electrons on the surface of metals, which is a good way to guide light propagation in a small size. Plasmonic waveguides, however, suffers from severe losses. Zhang *et al* predicted that losses could be greatly reduced by controlling the hybridization of the fundamental mode of a dielectric cylinder with the surface plasmon polaritons (SPP) of a dielectric-metal interface.²⁰⁹ In another paper, they experimentally demonstrated the plamonic laser by using a hybrid plasmonic waveguide consisting of a CdS nanowire and a silver surface with 5 nm gap.²¹⁰ Lu *et al* demonstrated a similar plasmonic laser in the hybrid structure of GaN/GaInN core-shell NW and Ag film.²¹¹

Figure 7-2. (a) Dark field optical image of the DMD (dielectric-metal-dielectric) coupling device (left). Optical image of the intensity map of the device with (middle) and without (right) the bridging Ag nanowire. Taken from Ref.195. (b) Schematic of a single InGaN/GaN core-shell nanorod on an Ag film (28 nm thick). Taken from Ref. 211. (c) The energy-density distribution of (b) calculated by the eigenmode method. (d) SEM image of a ZnO comb structure. (e) Far-field optical image of spatially resolved light emission from individual nanowires of the comb structures. (f) Power-dependent emission spectra recorded on the comb structure. From bottom up, the excitation energy densities are 252, 505, 580, 707, 883 nJ/cm², respectively. Taken from Ref. 198.

Future research may be correlated to two directions: one is the development of low-cost methods to assemble semiconductor nanowires into functional devices with high throughput; the other is the growth of rational heterojunctions consisting functional components on demand. For the IO/ITO nanowires, the fabrication process and structural property have been studied extensively. Further research may be the application of guided IO/ITO nanowires in sensors, solar cells and displays. Because

of their high conductivity, transparency and tunable carrier density, ITO/IO NWs can be used as electrode and functional components. Figure 7-3 shows the possible ways to use ITO/IO NWs as detector and transparent electrodes.

Figure 7-3. Applications of guided ITO/IO NWs. (a) Schematic illustrating the applications of planar ITO/IO NWs in sensors/transparent electrodes. (b) Schematic illustrating the growth of transparent ITO electrodes with 3D architecture. Such architecture can be used in solar cells as expressway of electron collection.

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Appendix 1. Derivation of Gibbs-Thomson Effect Equations for Planar Nanowires

Schematics illustrating the growth mechanism of ITO NWs

◆ **Model (a):**

The volume of NW can be written as:

$$V = r \times 2r \times L = 2r^2L$$

When the length L increases to $L+\Delta L$, the volume change can be written as:

$$\Delta V = 2r^2\Delta L$$

So the atom number change is written as:

$$\Delta N = \frac{\Delta V}{\Omega} = \frac{2r^2\Delta L}{\Omega} \quad (a1)$$

The Gibbs free energy changes during NWs growth can be expressed as:

$$\Delta G = \Delta N (-\Delta\mu_0) + \Delta S_{vs}\alpha_{vs} + \Delta S_{inter}\alpha_{inter} - \Delta S_{inter}\alpha_{ysz} \quad (a2)$$

The supersaturation is given as:

$$\Delta\mu = -\frac{\Delta G}{\Delta N} = \Delta\mu_0 - \frac{\Delta S_{vs}\alpha_{vs} + \Delta S_{inter}\alpha_{inter} - \Delta S_{inter}\alpha_{ysz}}{\Delta N} \quad (a3)$$

We know:

$$\Delta S_{vs}\alpha_{vs} = 4r\Delta L \times \alpha_{vs,(100)}$$

$$\Delta S_{inter}\alpha_{inter} = 2r\Delta L \times \alpha_{inter,(100)}$$

$$\Delta S_{inter}\alpha_{ysz} = 2r\Delta L \times \alpha_{ysz,(100)}$$

Substitute these equations into (a3) and the supersaturation is re-written as:

$$\Delta\mu = \Delta\mu_0 - \frac{\Omega}{d}(4\alpha_{vs,(100)} + 2\alpha_{inter,(100)} - 2\alpha_{ysz,(100)}) \quad (a4)$$

◆ **Model (b):**

The volume of NW can be written as:

$$V = r \times 2r \times L = 2r^2L$$

When the length L increases to L+ΔL, the volume change can be written as:

$$\Delta V = 2r^2\Delta L$$

So the atom number change is written as:

$$\Delta N = \frac{\Delta V}{\Omega} = \frac{2r^2\Delta L}{\Omega} \quad (b1)$$

The Gibbs free energy changes during NWs growth can be expressed as:

$$\Delta G = \Delta N (-\Delta\mu_0) + \Delta S_{vs}\alpha_{vs} + \Delta S_{inter}\alpha_{inter} - \Delta S_{inter}\alpha_{ysz} \quad (b2)$$

The supersaturation is given as:

$$\Delta\mu = -\frac{\Delta G}{\Delta N} = \Delta\mu_0 - \frac{\Delta S_{vs}\alpha_{vs} + \Delta S_{inter}\alpha_{inter} - \Delta S_{inter}\alpha_{ysz}}{\Delta N} \quad (b3)$$

We know:

$$\Delta S_{vs}\alpha_{vs} = 2r\Delta L \times \alpha_{vs,(110)} + 2r\Delta L \times \alpha_{vs,(100)}$$

$$\Delta S_{inter}\alpha_{inter} = 2r\Delta L \times \alpha_{inter,(110)}$$

$$\Delta S_{inter}\alpha_{ysz} = 2r\Delta L \times \alpha_{ysz,(110)}$$

Substitute these equations into (b3) and the supersaturation is re-written as:

$$\Delta\mu = \Delta\mu_0 - \frac{\Omega}{d}(2\alpha_{vs,(100)} + 2\alpha_{vs,(110)} + 2\alpha_{inter,(110)} - 2\alpha_{ysz,(110)}) \quad (b4)$$

◆ **Model (c):**

The volume of NW can be written as:

$$V = \frac{1}{2} \times r \times 2r \times L = r^2L$$

When the length L increases to L+ΔL, the volume change can be written as:

$$\Delta V = r^2\Delta L$$

So the atom number change is written as:

$$\Delta N = \frac{\Delta V}{\Omega} = \frac{r^2 \Delta L}{\Omega} \quad (c1)$$

The Gibbs free energy changes during NWs growth can be expressed as:

$$\Delta G = \Delta N (-\Delta\mu_0) + \Delta S_{vs}\alpha_{vs} + \Delta S_{inter}\alpha_{inter} - \Delta S_{inter}\alpha_{ysz} \quad (c2)$$

The supersaturation is given as:

$$\Delta\mu = -\frac{\Delta G}{\Delta N} = \Delta\mu_0 - \frac{\Delta S_{vs}\alpha_{vs} + \Delta S_{inter}\alpha_{inter} - \Delta S_{inter}\alpha_{ysz}}{\Delta N} \quad (c3)$$

We know:

$$\Delta S_{vs}\alpha_{vs} = 2 \times \sqrt{2}r\Delta L \times \alpha_{vs,(100)}$$

$$\Delta S_{inter}\alpha_{inter} = 2r\Delta L \times \alpha_{inter,(110)}$$

$$\Delta S_{inter}\alpha_{ysz} = 2r\Delta L \times \alpha_{ysz,(110)}$$

Substitute these equations into (c3) and the supersaturation is re-written as:

$$\Delta\mu = \Delta\mu_0 - \frac{\Omega}{d} (4\sqrt{2}\alpha_{vs,(100)} + 4\alpha_{inter,(110)} - 4\alpha_{ysz,(110)}) \quad (c4)$$

◆ Model (d):

As shown in the following Figure, the cross section of (111)-W NW is hexagonal with sidewall of {113} planes. Because the angle formed by (111) and (1-13) planes is 121.5°, very close to 120°. In order to simply the calculation, we assume the angle between the top plane and side wall is 120° and the hexagonal is a regular hexagonal.

So the volume of NW can be written as:

$$V = 6 \times \left(\frac{1}{2} \times r \times \frac{\sqrt{3}}{2} r\right) \times L = \frac{3\sqrt{3}}{2} r^2 L$$

When the length L increases to L+ΔL, the volume change can be written as:

$$\Delta V = \frac{3\sqrt{3}}{2} r^2 \Delta L$$

So the atom number change is written as:

$$\Delta N = \frac{\Delta V}{\Omega} = \frac{\frac{3\sqrt{3}}{2} r^2 \Delta L}{\Omega} \quad (d1)$$

The Gibbs free energy changes during NWs growth can be expressed as:

$$\Delta G = \Delta N (-\Delta\mu_0) + \Delta S_{vs} \alpha_{vs} + \Delta S_{inter} \alpha_{inter} - \Delta S_{inter} \alpha_{ysz} \quad (d2)$$

The supersaturation is given as:

$$\Delta\mu = -\frac{\Delta G}{\Delta N} = \Delta\mu_0 - \frac{\Delta S_{vs} \alpha_{vs} + \Delta S_{inter} \alpha_{inter} - \Delta S_{inter} \alpha_{ysz}}{\Delta N} \quad (d3)$$

We know:

$$\Delta S_{vs} \alpha_{vs} = 4 \times r \Delta L \times \alpha_{vs,(113)} + r \Delta L \times \alpha_{vs,(111)}$$

$$\Delta S_{inter} \alpha_{inter} = r \Delta L \times \alpha_{inter,(111)}$$

$$\Delta S_{inter} \alpha_{ysz} = r \Delta L \times \alpha_{ysz,(111)}$$

Substitute these equations into (d3) and the supersaturation is re-written as:

$$\Delta\mu = \Delta\mu_0 - \frac{\Omega}{d} \left(\frac{16}{3\sqrt{3}} \alpha_{vs,(113)} + \frac{4}{3\sqrt{3}} \alpha_{vs,(111)} + \frac{4}{3\sqrt{3}} \alpha_{inter,(111)} - \frac{4}{3\sqrt{3}} \alpha_{ysz,(111)} \right) \quad (d4)$$

◆ Model (e):

When the length of (111)-R is L, the width is $L/\sqrt{3}$ according to the rhombohedral geometry relationship. The surface area and volume of NW can be written as:

$$S = L \times \frac{L}{2\sqrt{3}} + 4 \times \frac{L}{\sqrt{3}} \times (2r) = \frac{1}{2\sqrt{3}} L^2 + \frac{2}{\sqrt{3}} Lr$$

$$V = r \times L \times \frac{L}{2\sqrt{3}} = \frac{1}{2\sqrt{3}} r L^2$$

When the length L increases to $L+\Delta L$, the surface area and volume changes can be written as:

$$\Delta S = \frac{1}{\sqrt{3}} L \Delta L + \frac{2}{\sqrt{3}} r \Delta L \approx \frac{1}{\sqrt{3}} L \Delta L \quad (\text{because } L \gg r)$$

$$\Delta V = \frac{1}{\sqrt{3}} r L \Delta L$$

So the atom number change is written as:

$$\Delta N = \frac{\Delta V}{\Omega} = \frac{\frac{1}{\sqrt{3}} r L \Delta L}{\Omega} \quad (e1)$$

The Gibbs free energy changes during NWs growth can be expressed as:

$$\Delta G = \Delta N (-\Delta\mu_0) + \Delta S_{vs}\alpha_{vs} + \Delta S_{inter}\alpha_{inter} - \Delta S_{inter}\alpha_{ysz} \quad (e2)$$

The supersaturation is given as:

$$\Delta\mu = -\frac{\Delta G}{\Delta N} = \Delta\mu_0 - \frac{\Delta S_{vs}\alpha_{vs} + \Delta S_{inter}\alpha_{inter} - \Delta S_{inter}\alpha_{ysz}}{\Delta N} \quad (e3)$$

We know:

$$\begin{aligned} \Delta S_{vs}\alpha_{vs} &= \frac{1}{\sqrt{3}} L\Delta L \times \alpha_{vs,(111)} \\ \Delta S_{inter}\alpha_{inter} &= \frac{1}{\sqrt{3}} L\Delta L \times \alpha_{inter,(111)} \\ \Delta S_{inter}\alpha_{ysz} &= \frac{1}{\sqrt{3}} L\Delta L \times \alpha_{ysz,(111)} \end{aligned}$$

Substitute these equations into (e3) and the supersaturation is re-written as:

$$\Delta\mu = \Delta\mu_0 - \frac{\Omega}{d} (2\alpha_{vs,(111)} + 2\alpha_{inter,(111)} - 2\alpha_{ysz,(111)}) \quad (e4)$$

Appendix 2. Derivation of Growth Direction for Nanocone-Nanowire Kinked Nanostructures

◆ Type-I Kinked Nanostructures:

In order to derive the growth direction for both the NC base and the NW tip, we take two SAED patterns collected in two zone axis, such as $[001]$ and $[110]$. The results are shown in Figure S1.

Figure S1. (a,b) TEM images of the type-I NC-NW kinked nanostructure collected in $[001]$ and $[110]$ zone axis, respectively. The false color arrays indicate the corresponding observed directions. Scale bar: 200 nm. (c,d) Schematic showing the possible correct growth directions for NC base observed in $[001]$ and $[110]$ zone axis, respectively. (e,f) Schematic showing the possible correct growth directions for NW tip observed in $[001]$ and $[110]$ zone axis, respectively.

For the NC base, when the zone axis is $[001]$ (see Figure S1a), the observed growth direction (**which is not the correct growth direction**) is $[110]$. As shown in Figure S1c, the blue array or the yellow array or the green array might be the correct

growth direction. We don't know the correct growth direction. But we know the correct growth direction is in the black plane and the index of the black plane is (1-10). In the meanwhile, when the zone axis is [110] (see Figure S1b), the observed growth direction is [-111]. As shown in Figure S1d, the blue array or the yellow array or the green array might be the correct growth direction. We don't know the correct growth direction. But, similarly, we know the correct growth direction is in the black plane and the index of the black plane is (1-12). **As a result, the correct growth direction should be the intersecting line of (1-10) and (1-12) planes.**

Here we use a Wulff Net to help us find out the correct growth direction. The (1-10) plane can be represented by blue line in Figure S2a. Because of the symmetry in a cubic structure, there are two equivalent blue lines in Figure S2a. Similarly, the (1-12) plane can be represented by the four equivalent green curves. The intersecting points of these two types of curves are the intersecting lines of (1-10) and (1-12) planes. In Figure S2a, there are 8 intersecting points, denoted by red dots. Because of the symmetry in a cubic structure, there are only two effective intersecting points ([1-10], [-110], [110] and [1-10] are equivalent; [1-11], [111], [-111] and [-1-11] are equivalent). So the correct growth direction of NC base is [110] or [111]. From the SEM observation in Figure 1a, we know the NC was grown vertically from (111) substrate. And the XRD result shows there is only a (111) peak for as-fabricated NC-NW kinked structure. So the correct growth direction of NC base is [111].

For the NW tip, we use the same method to derive the growth direction of NW

tip. When the zone axis is $[001]$ (see Figure S1a), the observed growth direction is $[100]$. As shown in Figure S1e, the blue array or the yellow array or the green array might be the correct growth direction. We don't know the correct growth direction. But we know the correct growth direction is in the grey plane and the index of the grey plane is (010) . When the zone axis is $[110]$ (see Figure S1b), the observed growth direction is $[-112]$. As shown in Figure S1f, the blue array or the yellow array or the green array might be the correct growth direction. We don't know the correct growth direction. But, similarly, we know the correct growth direction is in the grey plane and the index of the grey plane is $(1-11)$. **As a result, the correct growth direction should be the intersecting line of (010) and $(1-11)$ planes.**

In the Wulff Net (see Figure S2b), the (010) plane can be represented by blue line. Because of the symmetry in a cubic structure, there are two equivalent blue lines in Figure S2a. Similarly, the $(1-11)$ plane can be represented by the four equivalent green curves. The intersecting points of these two kinds of curves are the intersecting lines of (010) and $(1-11)$ planes. In Figure S2b, there are 4 intersecting points (denoted by red dots). Because of the symmetry in a cubic structure, there is only one effective intersecting point ($[0-11]$, $[101]$, $[011]$ and $[-110]$ are equivalent). So the correct growth direction of NC base is $[011]$.

Figure S2. (a,b) Wulff Net of a cubic structure. The blue curves and green curves represent the corresponding planes in Figure S1c-f. The intersecting points, denoted by red dots, are the intersecting lines between the two planes represented by blue and green curves.

◆ **Type-II Kinked Nanostructures:**

In the type-II NC-NW kinked nanostructures, we use the similar method to derive the growth direction of every segments. We take two SAED patterns collected in two zone axis, such as $[110]$ and $[111]$. The results are shown in Figure S3a-b.

For the NC base, when the zone axis is $[110]$ (see Figure S3a), the observed growth direction is $[1-11]$. We don't know the correct growth direction. But we know the plane which contains the correct growth direction is $(1-1-2)$. The vector of this plane is indicated by red arrow in Figure S3a. Meanwhile when the zone axis is $[111]$ (see Figure S3b), the observed growth direction is $[2-1-1]$. Similarly, we don't know the correct growth direction. But we know the plane which contains the correct growth direction is $(0-11)$. The vector of this plane is indicated by red arrow in Figure S3b. **As a result, the correct growth direction should be the intersecting line of $(1-1-2)$ and $(0-11)$ planes.**

Figure S3. (a,b) TEM images of the type-II NC-NW kinked nanostructure observed in [001] and [110] zone axis, respectively. Scale bar: 200 nm. The false color arrays indicate the corresponding directions.

We use a Wulff Net to help us find out the correct growth direction of NC base. The (1-1-2) plane can be represented by blue lines in Figure S4a. Because of the symmetry in a cubic structure, there are four equivalent blue lines in Figure S4a. Similarly, the (0-11) plane can be represented by the four equivalent green curves. The intersecting points of these two types of curves are the intersecting lines of (1-1-2) and (0-11) planes. In Figure S4a, there are 12 intersecting points, indicated by red dots. Because of the symmetry in a cubic structure, there are only two effective intersecting points: [111] and [311]. From the SEM tilted-view image in Figure 1a, we know the NC grow vertically from (111) substrate. And the XRD results show there is only (111) peak for as-fabricated NC-NW kinked structure. So the correct growth direction of the NC base is [111].

For the connection segment between NC base and nanowire tip, we use the same method. When the zone axis is [110] (see Figure S3a), the observed growth direction is [1-10]. We don't know the correct growth direction. But we know the plane, which includes the correct growth direction, is (001). The vector of this plane is indicated by red arrow in Figure S3a. Meanwhile when the zone axis is [111] (see Figure S3b), the observed growth direction is [1-10]. Similarly, we don't know the correct growth direction either. But we know the plane, which includes the correct growth direction, is (-1-12). The vector of this plane is indicated by red arrow in Figure S3b. **As a result, the correct growth direction should be the intersecting line of (001) plane and (-1-12) plane.**

Figure S4. (a-c) Wulff net of a cubic structure. The blue curves and green curves represent the corresponding planes in Figure S3a,b. The intersecting points, indicated by red dots, are the intersecting lines between the planes represented by blue and green curves.

We use a Wulff Net to help us find out the correct growth direction of the connection segment. The (001) plane can be represented by blue circle in Figure S4b. Similarly, the (-1-12) plane can be represented by the four equivalent green curves. The intersecting points of these two kinds of curves are the intersecting lines of (001) plane and (-1-12) plane. In Figure S4b, there are four intersecting points, indicated by red dots. Because of the symmetry in a cubic structure, there is only one effective intersecting point: [110]. So the correct growth direction of connection segment is [110].

For the NW tip, we use the same method. When the zone axis is [110] (see Figure S3a), the observed growth direction is [3-3-2]. We don't know the correct growth direction. But we know the plane, which contains the correct growth direction, is (1-13). The vector of this plane is indicated by red arrow in Figure S3a. In the meanwhile, when the zone axis is [111] (see Figure S3b); the observed growth direction is [1-21]. Similarly, we don't know the correct growth direction. But we know the plane, which includes the correct growth direction, is (10-1). The vector of this plane is indicated by red arrow in Figure S3b. **As a result, the correct growth direction should be the intersecting line of (1-13) and (10-1) planes.**

We use a Wulff Net to help us find out the correct growth direction of NW tip. The (1-13) plane can be represented by blue curves in Figure S4c. Because of symmetry in cubic structure, there are four equivalent blue curves. Similarly, the (10-1) plane can be represented by the four equivalent green curves. The intersecting points of these

two kinds of curves are the intersecting lines of (1-13) and (10-1) planes. In Figure S4c, there are 16 intersecting points, indicated by red dots. Because of the symmetry in a cubic structure, there are only two effective intersecting points: [211] and [411]. So the correct growth direction of NW tip is [211] or [411]. From the SEM observation in Figure 6-1 and Figure 6-2, we know the NW tip forms an angle of 118° with the NC base. We already know the growth direction of the NC is [111]. So the growth direction of NW is [211] (the angle between [111] and [2-11] is 62°).

Because of the complexity of the type-II kinked structure, we chose another sample and do SEAD under a different zone axis. This time we choose [110] and [001] as zone axis.

As shown in Figure S5, we collect the SEAD patterns in two zone axis: [110] and [001]. The observed growth directions of different segments are indicated in Figure S5a,b, respectively. For the NC base, we know the two planes, which contain the observed growth directions, are (-112) under [110] zone axis and (-110) under [001] zone axis (indicated by red arrows). So the correct growth direction is the intersecting line of (-112) and (-110) planes. We use a Wulff Net to find out the intersecting line. In Figure S6a, we know the correct growth direction is [111] or [110]. Combining with the SEM observation in Figure 6-1 and XRD results in Figure 6-2, we know the correct growth direction of NC is [111].

For connection segment, we know the correct growth direction is the intersecting line between plane (-111) and plane (-100) (see Figure S5a-b). In Figure S6b, we know that the intersecting line is [110]. So the correct growth direction of connection

segment is $[110]$.

Figure S5. (a,b) TEM images of the type-II NC-NW kinked nanostructure collected in $[001]$ and $[110]$ zone axis, respectively. The false color arrays indicate the corresponding directions. Scale bar: 200 nm.

For NW tip, we know the correct growth direction is the intersecting line between $(-11-1)$ and $(-1-10)$ planes (see Figure S5a-b). In Figure S6c, we know that the intersecting line is $[112]$ or $[110]$. Because the growth direction of connection segment is $[110]$; the growth direction of NWs segment is $[112]$.

The results derived from this sample are consistent with the results derived from last sample, which prove the reliability of our approach for such highly kinked structures.