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**OXIDE SEMICONDUCTOR NANOWIRES
AND
SI-BASED NANOMATERIALS:
SYNTHESIS AND PROPERTIES**

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Oxide Semiconductor Nanowires And Si-based Nanomaterials: Synthesis and Properties

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Abstract

Title of Dissertation: OXIDE SEMICONDUCTOR NANOWIRES AND
 SI-BASED NANOMATERIALS: SYNTHESIS AND
 PROPERTIES

Zhang Zhou, Doctor of Philosophy, 2010

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

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The main objective of this dissertation is to extend the understanding of nanofabrication mechanisms and achieve controlled synthesis of functional nanomaterials with predesigned morphologies and properties, which are potential candidates of building blocks for future nanodevices and nanomachines.

Thanks to the fast growth of material characterization techniques, especially the developments of non-optical microscopes (such as scanning tunneling microscope, atomic force microscope, electron microscope, etc.), lots of interests have been drawn to nanomaterials in the recent decades. Aside from their intrinsic advantage of small size which warrants non-replaceable applications in specific areas, nanomaterials also possess many outstanding physical and chemical properties compare to the bulk and film

counterparts. However, industrial applications of nanomaterials are still limited due to the lack of knowledge in nanoscale dynamics, nanofabrication techniques, etc. Thus systematic studies are motivated to achieve reliable methods of nanomaterial synthesis with high quality and prominent properties.

In this dissertation, we studied the fabrication of several metal oxide and silicide nanomaterials (in particular, ZnO, SnO₂, MgO, Cu₃Si, and Mg₂SiO₄), using a simple method of vapor transport. Various nanostructures (e.g. nanowires, nanobelts, nanoparticles, nanoneedles, and nanonails) were obtained. Their morphologies and properties could be controlled by chemical compositions, growth mechanisms, and other experimental parameters.

The growth of ZnO nanowires was introduced as the first example. ZnO is a wide bandgap semiconductor with prominent properties. ZnO nanostructures have drawn a lot of interests in the recent decades due to potential applications in nanoscale electronic, photonic, energy conversion devices, etc. Systematic studies were performed on the growth of ZnO nanowires via a vapor transport method. The performance of various catalysts (Au, Pt, & Ag), sources and temperatures (ZnO + graphite, 800 °C; Zn, 500 °C) were compared. The competitions between vapor-liquid-solid and vapor-solid growth mechanisms are heavily affected by the growth parameters, resulting in different morphologies and structures with strong contrast in physical properties.

On another aspect of growth, modifying the powder source proves to be an effective method to tailor the as-grown morphology of the nanomaterials as well as their physical and chemical properties. As an example, Cu doped ZnO nanostructures were fabricated by adding CuCl₂ into Zn source powders before vapor transport growth. As a result,

needle and nail like nanostructures were obtained instead of nanowires (that are otherwise obtained by using pure Zn source powder). By tuning the experiment parameters (e.g. setup geometry), continuous morphology evolution of ZnO nanoneedle to nanonail was obtained on one single substrate (lateral dimension ~ 7 mm).

Similar strong doping effect on product morphologies was also observed in Ti doped SnO_2 nanostructures. Pure SnO_2 nanowires can be grown by vapor transport method using SnO_2 mix graphite powder as source. However, doping Ti by adding TiO_2 into the source powder can reliably convert the product structure to nanobelt, albeit the low doping rate. The growth mechanism is then altered, evidenced by the drastic changes in preferred growth directions and surface planes. Carefully tuning other experiment parameters (e.g. temperature, ambient, etc.) enables a fine control of the sizes of both undoped nanowires and Ti-doped nanobelts over 2 orders of magnitude.

Besides metal oxide nanomaterials, we have also put a lot of efforts on silicide related nanostructures, which are closely related to the current semiconductor industries. Using Au nanoparticles as catalysts, Cu_3Si and Mg_2SiO_4 nanostructures were epitaxially synthesized on Si wafers via the vapor transport route. Interestingly, the as-grown nanostructures exhibit self-assembled features and substrate-orientation-dependent morphologies. Cu_3Si nanotriangles, nanosquares, and nanowires were grown on Si (111), (100), and (110) substrates, respectively. On the other hand, Mg_2SiO_4 nanowires were aligned along one, two, and three specific directions (i.e. Si $\langle 110 \rangle$) on the surface plane of Si (110), (100), and (111) substrates, respectively. Au nanoparticles played key roles in these experiments. Besides absorbing source vapor, Au nanoparticles break the barrier of native oxide layer on the substrates, which is essential to the growth of Cu_3Si

nanostructures. In the synthesis of Mg_2SiO_4 nanowires, Au droplets (melt from nanoparticles at high temperatures) migrate on the substrate surface along specific directions, thus leading to the growth of the in-plane self-aligned nanowires.

Our studies extended the fundamental understanding on the growth mechanisms of nanostructures, and showed that there are plenty novel opportunities to tailor their morphology and properties. Such findings complement the traditional knowledge on thin film growth, and show that the nanomaterials synthesis is a fertile playground for both fundamental studies and potential applications. Our experience on controlled growth of nanostructures will also be important guidance for the design and fabrication of novel nanomaterials and functional nanodevices in future.

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Chapter 1

Introduction

§ 1.1 Overview on Nanoscience and Nanotechnology

Nanomaterials, generally referred as the group of materials with at least one dimension smaller than a few hundred nanometers, attracted substantial interest for the past few decades.^[1] The magnification of conventional optical microscope is limited by the optical wavelength (e.g., visible light: 380~750 nm), which became the major obstacle in the old days that hindered people's curiosity in the beauty of nanoworld. The invention of scanning tunneling microscope (STM, 1981), which provides direct observation on nanostructures, proves to be a milestone due to the breakthrough in magnifications that enable direct observations of nanoscale morphologies and structures.

The Nobel Prize discoveries of fullerene (C₆₀) and carbon nanotubes (CNT) marked the outburst of nanosciences.^[2-3] Scientists are now able to synthesize nanomaterials with various morphologies and hierarchical structures (e.g. 0D: nanoparticle, 1D: nanowire, 2D: thin film, and heterostructures) as well as compositions (e.g. metal, semiconductor, superconductor, organic, etc.). Although most of their applications are still at research level and not yet ready for wide-scale commercial, we can already foresee their great impacts on science and technology that would dramatically change our life style.

The evolution of semiconductor and IT industries is a good example. The chips that empower the electronic devices (such as computer and cell phone) are smaller and faster nowadays, thanks to the ever growing integration scale of the transistors, which doubles

Figure 1-1 CPU Transistor Counts 1971-2008 & Moore's Law (Source: Wikipedia).

nearly every two years, as predicted by Moore's Law (Figure 1-1). The size of a single transistor in state-of-the-art devices has reduced to nanoscale and sub-30 nm fabrication techniques have already been widely adopted. Owing to the developing nanoscience and semiconductor technology, the calculation power and storage capacities of a modern mobile phone can be much larger than some old super computers which occupied whole rooms.

Nanomaterials and nanodevices show potential applications in many key technological areas, including energy, environment, medicine, etc. Unique technologies were obtained in the development of nanoscience, which play irreplaceable roles that

benefit the scientific research and industrial applications. On the other hand, high quality nanomaterials are also important for the fundamental researches, such as studying the physical dynamics and chemical reaction mechanisms at nanoscale. The movement of objects obeys the Newton's Laws at the macroscopic scale, which is totally different from the quantum phenomena in atomic and sub-atomic scales. The nanoscale behavior should be considered as transition between the two, which are, however, complicated and theoretically difficult to study. Thus high quality nanomaterials are one of the best platforms for the fundamental studies in this specific area.

Studying nanoscience and developing nanotechnologies will affect how people live in general. Take the modern life science as an example, virus is the smallest creature observed so far, and exhibits nanostructured morphologies. For example, the H1N1 flu virus shows nanowire structures.^[4] In a more general context, the basic building blocks of living things are all nanostructured organic molecules, such as protein, DNA, etc. Thus the fundamental studies in nanoscience along with improving nanotechnologies help us to understand the living beings better and fight against diseases more efficiently.

In summary, nanoscience and nanotechnology are new branches in natural sciences. The potential application of nanomaterials and their irreplaceable importance in fundamental studies motivate us to contribute in this promising researching field.

§ 1.2 Advantages and Applications of Nanomaterials

Compared to their bulk counterparts, nanomaterials show advantages of unique properties and applications. Firstly, they are small in size and can be used as building

blocks in large scale integrated devices. Devices smaller in size usually consumes fewer resources, in the aspects of both material and energy, and thus are more environmental friendly. On another aspect, devices fabricated with smaller building blocks and larger integration scales may show better performance and functionalities. For example, one direction in developing mass storage devices is to increase the storage density by reducing the size of unit storage cells. Nowadays, the size of storage cells in hard disk and flash memories can be as small as a few tens of nanometers, and their storage densities are larger than 10 gigabytes per gram. In comparison, some old-fashioned hard disks weighed over a ton but held a storage of less than 10 megabytes, e.g., IBM 350 produced in 1956.

Large surface to volume ratio is another unique property of nanostructures, which warrants applications such as high sensitivity sensors. For example, various semiconductor nanowires were reported to be excellent gas sensors.^[5] There are also reports on organic nanowire transistors that are sensitive enough to detect single molecules.^[6] As another example, the performance of catalysts can also be enhanced using nanostructured materials due to the large surface area.^[7-11] Nanocatalysts have been widely adopted in research and industry, e.g. catalysts made of small particles of metals such as platinum are used in the chemical and refining industries as well as in catalytic converters in automobile tailpipes.^[12]

Various structured nanomaterials have been realized experimentally from the basic nanoparticles (0D), nanowires (1D) and thin films (2D) to heterostructures with greater complexity, including nanobelts, nanotubes, nanotowers, nanoneedles, nanonails, etc.^[13-16] It is possible to construct complex and functional nano “buildings” designed for specific purposes. For example, Au nanocages were constructed for biomedical applications such

as drug delivery to targeted cancer cells.^[17] It is important to note that some specific applications show strong dependence on the morphologies and structures of nanomaterials. For example, thin nanowire arrays are more suitable for field emission applications.^[18-20] There are also reports on tunable wetting properties by nano-engineering the surfaces of materials.^[21-22]

Aside from pure geometric differences, size effects in nanomaterials may also induce some intrinsic properties which cannot be obtained from their bulk counterparts. As one or more dimensions are reduced to nanoscale, the materials can no longer be considered as a continuous medium, since the number of atoms allocated along these directions is limited (typically less than thousands). Quantum effects, which are size and morphology dependent, become remarkable strong in nanomaterials. For example, the color of Au nanoparticle suspension depends on the diameter of the particles, showing strong size dependent quantum effect on band energy deviations at nanoscale.^[23] However, no such effect is observed if Au particle have larger diameters.

Quantum effects, which are prominent and universal in nanomaterials, provide extra freedom in designing new materials and functional devices. Take the example of Au nanoparticle suspensions again,^[23] their colors are determined by the surface plasmon bands of the nanoparticles, which could be controlled by tuning the diameters. Similar phenomena have also been observed in nanostructure incorporated organic light emitting diodes.^[24-26]

Another good example is carbon based nanostructures, such as fullerene (C₆₀, 0D), carbon nanotube (CNT, 1D) and graphene (2D), which are among the most important low dimensioned materials and have been widely studied in the recent years.^[27-29] With basic

structures similar to sheets of graphite, these nano counterparts show distinct properties. Compared to graphite, C_{60} and CNT are more stable at high temperature in O_2 rich environment. The electron mobilities are enhanced in graphene, depending on the exact layer numbers. The structure of CNT can be conceptualized by wrapping a piece of graphene into a seamless cylinder. However, the conductivity of CNT depends on how this graphene is wrapped up (e.g., a zigzag structure) and it could show either conductor or semiconductor type transport properties.

Although most of the studies on nanomaterials are still fundamental and focusing on prototype devices, scientists have already stepped forward to design the revolutionary functional nanodevices, i.e. nanomachines and nanorobots.^[30-40] Nanorobots are devices ranging typically in size from 0.1~10 μm and constructed of nanoscale or molecular components. With obvious advantages and potential applications, especially in life and medical sciences, the technology of nanorobotics will greatly expand and improve our abilities in the microscopic world, on which the lives of all the living beings and the macroscopic nature are based.

Although the studies on designing and fabricating nanomachines and nanorobots are still preliminary, the future is convincing and bright. Nature has already provided excellent examples for us to study and imitate. Enzyme, DNA, RNA, and even independent creatures like virus can all be classified as nanomachines. These natural nanomachines seem like been carefully designed to carry out specific functions with super high precision and efficiency. For example, DNA duplication is vital to reproduction and heredity of the population, while RNA act as active nanomotors to transport the raw materials (i.e. amino and nucleic acids).

Our technology fails to compete with the wisdom of the nature on various aspects. Compare to man-made devices, the natural nanomachines may show outstanding advantages of high efficiency, extra precision, diverse functionality, environment friendly, etc. So far artificial nanorobots still remain largely in hypothetical concepts and lots of efforts are necessary before we can finally realize them. It is also our motivation to contribute to this research field, and to control the motion of metal nanoparticles as we will detail later.

§ 1.3 Challenges in Nanotechnology

The fantastic features and promising applications of nanomaterials come along with great challenges in research. First of all, nanomaterials are difficult to observe and handle since their sizes are too small for conventional optical microscopy. Although various tools (e.g. electron microscopy and atomic force microscopy) can be used for direct observation of nanostructures, they all have technical limitations on different aspects, not to mention the high prices of the equipments. For example, scanning electron microscope is not suitable for insulating specimens, and samples for transmission electron microscopy cannot be too thick. Details will be discussed in Chapter 2.

Precisely handling nanomaterials, especially in large quantities, is still an issue which is very challenging. For example, although thousands of publications have proved good performance of single nanowire devices such as transistors and memories,^[41] the difficulties in large scale assembly and integration impede their industrial applications. Although it is possible to manipulate single nanowires using mechanical probes or optical

tweezers,^[42-43] uniform assembly of nanowires on large area with high quantities has never been easy.

Novel physical phenomena and specific properties distinguished nanomaterials from their bulk counterparts. However, abundant boundaries (large surface area) and prominent quantum effects generate great difficulties in theoretical studies. Nanostructures (with typically more than 1000 atoms on each scale) prove to be too complicated to be precisely calculated using first-principle methods. Theoretical guidance on experiments is largely empirical or semiempirical, leading to confusions in this research field to some extent.

The challenges in nanoscience and technology also lie in the lack of a universal method to fabricate nanomaterials reliably and precisely as desired. Most of the conventional routes for bulk and film fabrication such as solid state reaction simply cannot be applied directly to the synthesis of nanomaterials.^[44] The mainstream nanofabrication routes can be roughly classified into two categories: top-down (e.g., lithography, etching, etc.) and bottom-up (e.g. vapor transport deposition, hydrothermal, etc.).^[45-46] Although many techniques have been developed for nanofabrication, they can only apply to a small group of specific materials. Our ability in controlled nanofabrication is still very limited.

For example, the vapor transport method has been widely adopted in nanomaterial research. Various nanostructures, such as nanowires, have been synthesized using this simple experimental setup.^[47-51] However, the limited choices of source materials and the narrow growth windows make the synthesis of complex compound nanostructures extremely difficult. To the best of our knowledge, the nanomaterials with the most complex compositions grown by this method include no more than 3 kinds of element.

The limited knowledge on growth mechanisms and dynamic procedures also induces difficulties in optimizing experiment parameters and developing new fabrication techniques.

In summary, although the potential applications of nanomaterials are promising and exciting, we are still far away from the ultimate goal of fabricating nanomachines that are competitive to the natural ones. Great challenges lie in all aspects of nanoscience and nanotechnology. Fundamental studies are required to achieve better understandings of the nanoscale physics and dynamic procedures. On the other hand, various technological problems need to be solved, such as characterizing, handling and fabricating nanomaterials and nanodevices.

§ 1.4 Core Theme and Outline of Thesis

Nanomaterials synthesis is the main theme of this thesis. Instead of the traditional top-down lithography approach, we focus on the bottom-up self-assembly approach as we will detail later. Such approaches do not entail expensive equipment and complicated procedures, and will make impact on the nanotechnology in general, although there are obstacles to overcome in order to integrate with traditional technologies, such as patterning the as-grown nanomaterials for the fabrication of integrated devices.

My research focuses on the fabrication of functional nanomaterials, such as wide bandgap semiconductor ZnO and SnO₂ nanowires, and Cu- and Mg-related silicide nanomaterials. In order to achieve controlled growth of these nanostructures, I put a lot of effort studying their growth mechanisms and the effects of tuning various experiment

parameters, such as catalyst, element doping, and substrate. Our work extends the understanding of dynamic procedures in bottom-up self-assembled nanomaterials synthesis, which may help the design and fabrications of novel nanomaterials and devices in future.

In Chapter 2 a brief introduction to the conventional nanotechnologies is given. Nanomaterials synthesis approaches can be divided into two categories, i.e., top down and bottom up. Top-down methods usually adopt lithography and etching techniques. They are widely used to fabricate nanodevices with desired patterns. Examples of bottom-up methods include solution based chemical synthesis and vapor deposition synthesis. Thermal vapor transport deposition method was used in our experiments. In this chapter several widely used characterization techniques related to our work are also introduced, i.e., atomic force microscope, scanning electron microscope, transmission electron microscope, energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and X-ray diffraction.

In Chapter 3 the fabrication of ZnO and SnO₂ nanomaterials is discussed. ZnO and SnO₂ are wide bandgap semiconductor materials with important applications. The growth of ZnO and SnO₂ nanostructures (e.g. nanowires) is relatively easy due to their anisotropic crystal structures. By vapor transport method, it is widely understood that catalyst assisted vapor-liquid-solid (VLS) and vapor-solid (VS) mechanisms compete in the growth of the nanomaterials. Mechanism control may strongly affect the size and structure of the as-grown nanomaterials.

In this chapter, we tried to control the growth mechanism by tuning various parameters. Firstly, we studied the effect of catalyst and source vapor pressure in the

growth of ZnO nanowires. By comparing the behavior of various catalysts (Au, Pt, and Ag) and source (ZnO + graphite, low vapor pressure; Zn, high vapor pressure), we conclude that melting catalyst droplets and low source vapor pressure are essential to VLS growth. Otherwise VS mechanism dominates the nanowire growth. Secondly, we studied the effect of element doping in nanomaterials synthesis. By Cu doping (adding CuCl₂ into source powder), ZnO nanoneedles and nanonails were obtained instead of nanowires (pure, no doping). The ZnO nanonails show similar structure of nanoneedles, but with extra hexagonal caps on top. The size of the cap, i.e. the evolution from ZnO nanoneedle to nanonail, is found to be affected by the source vapor pressure and oxygen partial pressure. In the growth of SnO₂ nanomaterials, we have also observed significant morphology modification by Ti doping. By adding TiO₂ into the source powder (SnO₂ + graphite), SnO₂ nanobelts were obtained instead of nanowires. We can also control the lateral size of SnO₂ nanobelts and nanowires in a very large range (about 2 orders of magnitude) by tuning other parameters such as oxygen partial pressure. It is believed that element doping induced surface energy modification is the origin of the structure change.

In the third part of this thesis, in Chapter 4, we introduced the self assembled in-plane fabrication of Cu- and Mg-related silicide nanomaterials on Si substrates. Silicide materials are important due to their applications in semiconductor devices. Since the crystal structures of most silicides are close to single crystal Si, it has been observed that some silicide nanostructures show self assembled features corresponds to specific Si crystal directions. However, controlling their position and size prove to be challenging. In our experiments, uniform Au nanoparticles were pre-spread on the Si substrates before vapor transport growth. By supplying Cu vapor at high temperature, Cu₃Si nanotriangles,

nanosquares, and nanowires were obtained on Si (111), (100), and (110) substrates, respectively. By supplying Mg vapor, in-plane Mg_2SiO_4 nanowires were grown on all substrates. These nanostructures show self assembled features with their side boundaries along Si $\langle 110 \rangle$ specific directions.

Substrate and catalyst play key roles in the fabrication of these silicide related nanomaterials. The substrates act as the source of Si atoms and control the morphology of the as-grown nanostructures due to the anisotropic diffusion in single crystal Si lattice. Au nanoparticles absorb the source vapors, which is typical in the conventional VLS mechanism. Besides, Au nanoparticles also play some unique roles which are critical in our experiments. In the growth of Cu_3Si , Au help to break the barrier of the native oxide layer on Si substrate, thus making the reaction between Cu vapor and Si possible under low vacuum. In the synthesis of Mg_2SiO_4 , Au nanoparticles melt and diffuse on the Si substrate, leading to the growth of Mg_2SiO_4 nanowires. The positions of these nanostructures are controlled by the Au nanoparticle catalysts.

Finally, we summarize the whole thesis in Chapter 5.

Chapter 2

Nanomaterial Synthesis and Characterization

§ 2.1 Conventional nanomaterial synthesis routes

Nanofabrication methods could be roughly categorized into two groups: top-down and bottom-up approaches. However, the fabrication of complex nanoscale heterostructures may involve a combination of both synthesis routes.

§ 2.1.1 Top-down Approaches

Top-down approaches indicate fabricating structures from raw materials with the same component but larger sizes such as bulk and film.^[52] For example, graphene could be acquired by peeling off from a piece of graphite using scotch tapes.^[53] However, most top-down fabrication methods require more advanced patterning tools and state-of-the-art equipments. A typical example is the fabrication of large scale integrated semiconductor devices such as CPU, which involves lithography, etching, and deposition processes. Below we give a brief introduction to these techniques.

Lithography

Lithography involves the patterning of materials into predesigned features. Several lithography techniques have been developed, such as photolithography, e-beam lithography (EBL), and focus ion beam lithography (FIL).^[54]

Photolithography can precisely transfer the (predesigned) patterns on a photomask to the photoresist deposited on the sample surface. This technique is simple and reliable. It is

Figure 2-1 Schematics illustrate the typical photolithography process using positive photoresist and contact mode.

idea for mass production and is widely used in semiconductor and IT industries. Typical process of photolithography approach is shown below (also see Figure 2-1):

1. Photoresist, which is sensitive to the working light source (e.g. 365 nm UV light generated by Hg lamp), is spin coated on the substrate wafer. The thickness of the photoresist is controlled by the spin speed. The liquid photoresist is then hardened by baking.
2. The substrate wafer is exposed to the working light source through a photomask with predefined features, which controls the transparency of the mask. Thus the

photoresist film is partly activated and the patterns on the photomask are transferred to it.

3. A specific chemical solution called developer is applied to the wafer, which selectively removes the exposed (i.e. positive photoresist) or unexposed (i.e. negative photoresist) part of the photoresist.

Now the features on the photomask are copied to the photoresist on the substrate and subsequent processes like etching or deposition can be performed. Photolithography is efficient in mass production but the resolution is limited by the optical wavelength of exposing light source. Typical resolution of the mask aligners using contact mode (photomask contact with substrate directly) is a few micrometers. State-of-the-art technologies have already pushed the resolution limited to less than one tenth of the wavelength (i.e. tens of nanometers). However, the high end equipments (mask aligner) are too expensive to be equipped by most labs.

The resolution problem can also be solved by replacing light with electron beams or ion beams, which have much shorter wavelengths. The electron-beam-lithography (EBL) system is usually integrated into a scanning electron microscope where the electron beams are focused and scanned on the sample surface. With electron sensitive resist material (e.g. polymethyl methacrylate) pre-deposited, the movement of the electron beam can be programmed to “draw” patterns on sample surfaces. Unlike photolithography, EBL is a mask free process with higher flexibility but lower efficiency (compare electron beam scanning to UV light exposure). EBL technique is widely adopted in R&D.

Focus ion beam (FIB) lithography is similar to EBL. Ion beam instead of e-beam is used. Since the momentum of accelerated ions are usually much higher than electrons

(because ions are much heavier than electrons), ion beam scanning on sample surface is more destructive. Thus it is possible to use the focus ion beam to derive direct surface engineering without the help of assistance materials such as photoresist. It can also be considered as a focused area dry etching technique.

Various new technologies for nano lithography have been invented in recent years, aiming at more economical and competitive approaches for the mass production of nanodevices. For example, nanosphere lithography uses uniform nanospheres to disperse on the substrate and form self-assembled close-packed patterns.^[55] The patterns normally exhibit hexagonal features and their sizes can be controlled by the diameters of the nanospheres. In another example, nano-printing technique is developed to print nano features directly on the (soft) substrate surface by providing a pressure on the (hard) mold.^[56-57] It is similar to the traditional printing method known as "gravure printing". These technologies are not yet matured and we are not going through the details here.

Etching.

Etching technologies are widely adopted in micro- and nano-fabrications. Nanostructures can be fabricated by etching through patterned features as mask, such as the patterns made on photoresist by photolithography. According to the type of etching media used, etching processes could be categorized into physical and chemical approaches. Plasmas (e.g. argon plasma) are common etching media in the physical etching processes, where the high energy ions work as the active agents to strike on the target materials and knock out the surface atoms.^[58] The plasma etching approaches are universal and suitable for most of the materials, although the etching rate depends

strongly on the target materials and the plasma sources. Since these processes usually take place in vacuum chambers, they are also categorized into dry etching approaches.^[59]

In chemical etching approaches, the etching mechanisms involve chemical reactions between the etching media and the target materials. Since various chemical solutions are commonly adopted as etching media, they are also called wet etching processes. Etching media is one of the most key factors in chemical etching because the medium must match the target material due to the selectivity of chemical reactions. Suitable etching media should be carefully chosen for high efficiency and good selectivity. For example, HF acid is commonly considered as the best etching media to remove silicon oxide efficiently while leaving the pure silicon wafer intact (with good etching selectivity).

Generally speaking, dry etching processes are universal. For example, plasma etching can be applied to most materials, although there is difference in etching rate. Dry etching also offers advantage of relatively high resolution. In plasma etching, the etching

Figure 2-2 Schematic illustrations showing the difference between vertical, isotropic and anisotropic etching processes.

direction can be well controlled by tuning the direction of the incident ion beams (by electric field, filter, etc.). Compared to dry etching, wet etching approaches are usually more economic, since they do not require expensive high vacuum chambers. However, each etching medium and process can only apply to specific target materials. There is no universal solution for wet etching. On the other hand, wet etching usually gives isotropic profiles (Figure 2-2), which limits the resolution of the patterns. Anisotropic etching can also be achieved by wet etching in some specific situations. For example, the etching speed along different crystal directions may vary in crystalline materials, inducing anisotropy in the etching profiles in single crystal material, such as single crystal Si wafer etched by potassium hydroxide (KOH) solution.^[60]

Deposition.

Deposition is not a top-down fabrication method. We put this section here to introduce some deposition techniques closely related to the nanofabrication process by lithography. The conventional physical deposition approaches suitable for R&D include thermal evaporation deposition,^[61] sputter deposition,^[62] pulsed laser deposition,^[63] etc.

Thermal evaporation deposition is suitable for materials with relatively low melting points such as metals (e.g. Au, Ti, etc.) and some inorganic compounds. The source materials are evaporated by thermal heating (or by electron beam, which is known as e-beam evaporation), and the source atoms or molecules are emitted and deposit on the substrate. Thermal evaporation deposition is generally considered a good approach with a well controlled deposition rate and high product quality. However, its applications are limited since most materials (e.g. most of the oxide compounds) cannot be thermally

evaporated due to high melting points, or low physical or chemical stability at high temperatures.

PLD and sputter deposition use pulsed laser (in the case of PLD) or plasma ions (sputter) to evaporate the target materials. As illustrated in Figure 2-3, a typical PLD setup includes a target holder and a substrate holder (usually with heater) mounted face to face in a high vacuum chamber. High energy laser pulses (e.g. KrF excimer laser, wavelength: 248 nm) are introduced into the chamber through a quartz window and focused on the target surface. The laser pulses help to break the chemical bonds in the target and plasma plumes containing ions from the target surface are generated. The vaporized target atoms are then deposited on the substrates.

PLD works well with most of the inorganic materials. However, organic materials cannot resist high energy laser beams, and thus are not suitable in PLD. The major advantage of the PLD approach is that it assures stoichiometric composition transport from the target materials to the substrates. Along with various other advantages such as

Figure 2-3 Schematics illustrating a typical pulsed laser deposition system.

good flexibility, controllability and excellent deposition quality, PLD techniques are widely adopted in the R&D. However, limited by the spot size of the laser beams, uniform deposition in large areas, which is important for mass production, is challenging in PLD technology.

The setup of sputter deposition is similar to PLD. High energy plasma ions (e.g. Ar ions), instead of laser pulses, are used to knock out the atoms from the surface of the target materials. The plasmas are generated by electric discharge (by DC, AC, or RF current) and confined near the target surface by magnetic field (usually from the magnet attached behind the target). The topology of the magnetic field may strongly affect the deposition quality such as the uniformity of the product film in large areas. Compared to PLD, sputter deposition is weaker at keeping the stoichiometric composition of the target materials. However, they also provide extra flexibility in this approach that expands its application in the R&D. On the other hand, the active deposition area is big enough to meet the requirement of mass production in industries.

§ 2.1.2 Bottom-up Approaches

Although the top-down nanofabrication approaches look straightforward, the actual processes are usually complicated and require expensive equipment, thus limiting their applications. Various new synthesis routes based on the bottom-up growth of the nanostructures are developed.^[45] Bottom-up fabrication involves the transport of source elements and the simultaneous growth of the product materials. The key factors are the dynamic mechanisms of source generation, transportation, and structure growth.

Figure 2-4 (a) Schematic illustrates the typical experiment setup of vapor transport growth. (b) Photo of a real system.

Vapor transport deposition is one of the most popular nanofabrication methods. With the advantages of simple equipment setup and high flexibility, numerous nanostructures with various compositions and morphologies have been successfully synthesized using this method. Most of the nanomaterials fabricated and studied in this thesis are also prepared through this route.

Typical experiment setup of vapor transport approach includes a horizontal tube furnace with vacuum and gas supply systems, as shown in Figure 2-4. Source materials are placed at the center of the working tube. Source vapors are generated at high

temperatures, due to thermal evaporation (e.g. $\text{Zn (s)} \xrightarrow{\Delta} \text{Zn (g)}$) or chemical reactions (e.g. $\text{ZnO (s)} + \text{C (s)} \xrightarrow{\Delta} \text{Zn (g)} + \text{CO (g)}$). Carrying gas is supplied and transports the source vapor downstream to deposit on the substrates. The carrying gas usually consists of inert components such as argon and nitrogen, but active agents like oxygen and hydrogen may also be added to meet specific experiment requirements. Sometimes the source elements can also be supplied directly in gas form, such as in metalorganic chemical vapor deposition systems.

The vapor transport nanofabrication approach is simple and flexible. However, most of the reported nanostructures prepared in this way have very simple compositions such as ZnO, SnO₂, and In₂O₃ nanowires.^[64-67] One of the challenges lies in the selection of proper source materials that generate two or more kinds of vapor at the same temperatures.

Figure 2-5 (a) Schematic illustrates the experiment setup of PLD assisted vapor transport nanowire growth. (b) SEM image of iron oxide nanowires fabricated by this method.^[68]

Vapor transport deposition is somehow a self-purifying process (similar to distillation). Even if it is somehow possible to generate several element vapors simultaneously, it does not guarantee that the product will show the phases of complex compositions. In most cases, separate simpler phases are more likely to occur from the entropy and free energy point of view. To the best of our knowledge, no nanocrystal with more than 3 elements in composition has ever been fabricated by vapor transport methods. Element doping appears feasible in most cases, but the doping rates are sometimes quite limited. Aside from the self-purifying mechanism, the challenges of element doping also lie in the fact that nanostructures have lower tolerance to defects and alien elements compared to their bulk counterparts.

To overcome the shortcomings of the conventional vapor transport method, PLD assisted vapor transport approach was proposed by Morber *et al.*^[68] As shown in Figure 2-5, high energy laser pulses are used to knock out the elements from the rigid source materials, which cannot be thermally evaporated at a reasonable temperature. Iron oxide nanowires were successfully fabricated using this method.

Other popular bottom-up nanofabrication methods include chemical vapor deposition,^[69] solution based (hydrothermal) and melting salt based fabrication approaches,^[70-71] etc. There are also reports using conventional thin film growth technologies to synthesis nanomaterials. For example, substrates with nanoengineered surface can be used as templates in the synthesis of nanostructures during the deposition processes. A well known example is the anodic aluminum oxide (AAO) template.^[72-73] Various nanostructures (e.g. nanowire, nanotube, nanoparticle, etc.) have been fabricated by depositing the target materials directly on the AAO templates. It is also possible to

growth nanostructures on substrates with flat surfaces. For example, using gold nanodroplets as catalyst can effectively change the crystal growth mode and induce the synthesis of nanostructured products such as MgO nanowires.^[74]

§ 2.2 Characterization Techniques

Nanostructures are too small to be observed directly using optical microscopes. Instead of light, electron, X-ray and atomic force could be used as the probes to explore the nano world. Typical examples include atomic force microscope, scanning electron microscope, transmission electron microscope, energy-dispersive X-ray spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy. Below we give brief introduction to some of the most widely used characterization techniques in nanoscience and technology.

§ 2.2.1 Atomic Force Microscope

Atomic Force Microscope (AFM) consists of a cantilever with a sharp tip (typically 20 nm) at the end which is used to scan on the sample surfaces, as shown in Figure 2-6. The cantilever deflects when external force (e.g. mechanical contact force and van der Waals force) exerts on it. The small bending is magnified by reflecting a laser beam, whose displacement (large enough due to the long optical path) is signaled by a position sensitive photo detector. Thus the surface profile of the sample is revealed by detecting the bending of the cantilever during the horizontal scanning. Theoretically there is no limit on the magnification of AFM, however, the unavoidable thermal vibrations restrict

Figure 2-6 (a) Schematic illustrates the working principle of AFM. The image shown on the holder is the surface height profile ($5 \times 5 \mu\text{m}$) of MgO (100) substrate after annealing at 1300°C for 24 h. (b) Photograph of a VEECO Dimensional-3100 AFM.

the resolution to $\sim 0.1 \text{ nm}$. There are also reports that specially designed AFM experiments can push the resolution to atomic scales.^[75] AFM can be used to acquire high resolution images of the sample surface. However, its application is limited when the surface is too rough. It is also not suitable for the samples with nanostructures not rigidly mounted to the substrates such as the out-of-plane nanowire arrays.

Besides the conventional contact mode (AFM tip is in constant contact with the sample surface during scanning), in which the cantilever drags directly on the surface and easily causes damages to both samples and scanning tips, tapping mode is popular. In this mode, the cantilever is driven to oscillate up and down (typically $\sim 100 \text{ nm}$) at near its resonance frequency and the interaction force is imaged when it scans close to sample surface. Tapping mode is gentler to the samples and tips. It is more reliable to imaging the surface morphologies with sharp steps. Besides, phase change of the oscillation due to the

interaction forces provides extra information of the samples, such as the stiffness of the sample. The contrast in phase helps to distinguish different compositions in the scanning area.

The conventional AFM measures record the van der Waals force between the cantilever and the sample surface. It can also be configured to measure other interactions for specific applications. For example, a magnetized cantilever can be used to measure the magnetic momentum on the sample surface, which is also known as magnetic force microscopy (MFM). Similarly, a charged AFM tip (CAFM mode) is able to sense the electric potentials.

Armed with piezoelectric element in modern AFM systems, the tip movement can be controlled to 1 nm in accuracy. Thus AFM can be also used as nano manipulator (known as “nanoman” mode). For example, it is possible to move nanoparticles and nanowires along predetermined tracks. If the AFM tip is harder than the sample material, it is also possible to “write” on the surface by scratching. By combining the nanoman mode with MFM or CAFM mode, we can “write” nanopatterns by magnetizing or oxidizing the sample surfaces.

§ 2.2.2 Scanning Electron Microscope

Scanning electron microscopy (SEM) images sample morphologies by electron beam (typically energy: 1~30 keV) scanning, which interacts with the atoms to produce signals containing information on surface topography, composition and other properties.^[76] The signals produced by injecting electron beams include secondary electrons, back-scattered

Figure 2-7 (a) Photograph of a JEOL JSM-6700F field emission SEM equipped with EDS accessory. (b) Typical SEM image showing a tree like ZnO structure composed of nanowires and tubes.

electrons (BSE), characteristic X-rays, photons (cathodoluminescence), etc.

The most common imaging mode collects the low-energy (<50 eV) secondary electrons which are ejected from the k-orbitals of the specimen atoms (within a few nanometers from the surface) by inelastic scattering interactions with beam electrons. The strength of the signal depends much on the angle between incident beam and the sample surface, resulting in images with a well-defined, three-dimensional appearance.

BSE, on the other hand, consists of high-energy electrons originating in the incident beam, which are reflected or back-scattered out of the interaction volume by elastic scattering interactions with specimen atoms. Since heavier elements backscatter electrons more strongly, BSE image shows high contrast between areas with different compositions. BSE can also image electron backscatter diffractions, which could be used to determine the crystallographic structure of the specimen.

The spatial resolution of SEM depends on the size of the electron spot, which in turn depends on both the wavelength of electrons (controlled by accelerating bias voltage) and the electron-optical system (like magnetic lens). Generally speaking, higher beam energy induces higher resolution, which falls into somewhere between less than 1 nm and 20 nm depending on the instruments. The resolution of SEM is good for observing the morphologies of nanomaterials, but not enough to see single atoms.

The specimens must be conductive to retrieve clear images by SEM. The incident electrons may accumulate on insulating surface, inducing local electric fields that may strongly affect the trajectories of secondary electrons and BSE. This charging effect significantly lowers the resolution by causing constantly drifting images and inaccurate boundary positions. On the other hand, charging effects are stronger with higher beam energies and larger beam currents, which are required for high magnification investigations. Charging effect can be mitigated by coating the specimen with conducting films like Au and graphite, however, permanent damages are induced this way and it is not suitable for applications like electron beam lithography.

§ 2.2.3 Transmission Electron Microscope

Transmission electron microscopy (TEM) is another electron imaging technique.^[77] High-energy electron beam is transmitted through ultra thin (typically $<1\ \mu\text{m}$ for low resolution imaging and $<100\ \text{nm}$ for high resolution imaging) specimen and diffracted. It is then magnified by magnetic lenses and focused onto an imaging device, such as fluorescent screen and CCD camera. TEM is capable of imaging at a significantly higher

Figure 2-8 (a) Photograph of a JEOL 2100F TEM system equipped with EDS accessory. (b–d) Typical low resolution, high resolution TEM images and corresponding SAED pattern taken from an indium tin oxide nanowire.

resolution than light microscopes, owing to the small de Broglie wavelength of electrons.

Theoretically, the maximum resolution δ that can be obtained by a microscope can be estimated by the classical Rayleigh criterion:

$$\delta = \frac{0.61\lambda}{\mu \sin \beta}$$

where λ is the wavelength of the radiation, μ is the refractive index of the viewing medium, and β is the semi-angle of collection of the magnifying lens. $\mu \sin \beta$ is called the numerical aperture. The wavelength of an electron depends on kinetic energy E . Consider the relativistic effects, as in TEM an electron's velocity approaches the speed of light, c . We have

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

where h is Planck's constant, m_0 is the rest mass of an electron. For a typical TEM equipped with a 100 keV electron source, the wavelength is ~ 4 pm ($1 \text{ pm} = 10^{-12} \text{ m}$). However, distortion introduced by lens assembly and many other disturbances (spherical and chromatic aberrations, astigmatism, etc.) all contribute to degrading the image quality and reducing the resolution. Today, typical TEMs using electron energy equal to or higher than 200 keV can achieve atomic scale resolution.

At low magnification mode, TEM image is constructed by the variation in electron absorptions due to differences in thickness and compositions of the specimen. At high magnification mode (enough to see single atoms), complex wave interactions modulate the intensity of the images that require expert analysis. Generally speaking, heavier elements induce stronger diffraction, and thus turn out to be darker in the images. With the help of professional software, it is possible to determine the specimen thickness by fitting the high resolution images with the simulated ones.^[78-79]

Using TEM, we can also obtain the electron diffraction patterns by changing the strength of the intermediate lens. Select area electron diffraction (SAED) pattern reflects the reciprocal space of the sample. It is useful to study the lattice structures of crystalline samples. SAED patterns contain more information than the fast Fourier transform (FFT) of the high resolution images, although they look similar. It is reported that, assisted by computer, SAED pattern can be used to further improve the high resolution image's quality and increase the resolutions.^[80]

TEM is one of the few characterization techniques (such as scanning tunneling microscope) with resolution high enough to see atomic lattices in crystalline materials. However, the requirement on the small thickness of the specimen limits its application.

For example, to obtain planar view TEM images of thin films, we need to polish the sample to remove the substrates and thinning the films. The sample will be very fragile (due to the small thickness). The sample preparation process usually requires expert experience and specific equipment such as focus ion beam cutter. The samples phase may also been modified during the mechanical polishing process or exposing to air and water.

§ 2.2.4 Energy-Dispersive X-ray Spectroscopy

Energy-dispersive X-ray spectroscopy (EDS) is an analytical technique used for elemental analysis and chemical characterization.^[81] The interaction between electromagnetic radiation and specimen is investigated by analyzing the emitted X-rays. Since each element has unique electron orbitals, the energies of the emitted X-rays due to the electron transitions are characteristic properties of different elements that can be used for element identification.

To stimulate the emission of characteristic X-rays, high energy particle beam (electron, proton, photon, etc.) is focused onto the sample. As illustrated in Figure 2-9(a), all the electrons are initially at ground state by occupying the lowest energy orbitals. One electron is excited by the incident particle and knocked out of the shell, thus generating a hole. Another electron (at higher energy orbital) jumps down to fill the hole, releasing energy in the form of an X-ray photon. The intensity and energy distribution of the X-rays can be measured by energy-dispersive spectrometer, which characterize the energy difference of the two shells. Thus the composition of the specimen can be precisely

Figure 2-9 (a) Schematics showing the principles of characteristic X-rays and EDS. (b) A typical EDS spectrum taken from a sample with $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin film deposited on MgO nanowire array substrate. (c) Corresponding black field TEM image and EDS element mappings.

determined from the X-ray spectrum.

EDS can be installed as an accessory in SEM and TEM systems, where the high energy electron beams stimulate the characteristic X-rays. Taking the advantages of simultaneous morphology observation in these microscopes, EDS is capable to retrieve the information of chemical composition from a small point (the focused area of the electron beam) instead of the whole sample. Thus element mapping is possible to show the spatial distributions of the elements (Figure 2-9(c)).

The accuracy of EDS technique is affected by several variants. Windows in front of

the detector can absorb low energy X-rays. Thus elements with atomic number less than 5 (i.e. H, He, Li, and Be) are not detectable. Elements may also have overlapping peaks (energy difference smaller than the resolution of the detector, e.g. Ti K β and V K α). Inhomogeneity and roughness of the specimen can also affect the accuracy of EDS detections. The sensitivity of EDS to different elements varies. Generally speaking, 1% atomic ratio can be considered as the limit of the resolution of EDS technique.

§ 2.2.5 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material.^[82] XPS spectra are obtained by irradiating materials with X-rays and simultaneously measuring the kinetic energy and number of electrons that escape from the top layer (1~10 nm) of the specimen. Because the energy of a particular X-ray wavelength is known, the binding energies of the emitting electrons can be determined from the following equation based on the work of Ernest Rutherford (1914):

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

where E_{binding} is the binding energy of the electron, E_{photon} is the energy of the X-ray photons, E_{kinetic} is the kinetic energy of the emitting electron and ϕ is the work function of the spectrometer (not the material).

Typical XPS spectra show plots of the number of electrons detected versus binding energy. Each element produces a characteristic set of XPS peaks at characteristic binding

energy values that identify its existence in or on the surface of the specimen. These characteristic peaks correspond to the electron configuration of the electrons within the atoms, i.e., 1s, 2s, 2p, 3s, etc. The number of detected electrons according to each peak is directly related to the amount of element within the area (volume) irradiated. To calculate the element concentrations, raw XPS peak counts should be corrected by dividing a “relative sensitivity factor” and normalized over all of the elements detected.

XPS can be used to measure:

- Elemental composition at sample surfaces (typically top layer of 1~10 nm);
- Empirical formula of pure materials;
- Elements that contaminate a surface;
- Chemical or electronic state of each element at the surface
- Uniformity of elemental composition across the top surface (i.e., line profiling or mapping);
- Uniformity of elemental composition as a function of ion beam etching (i.e., depth profiling).

Quantitative accuracy of XPS depends on several parameters, such as peak intensity, accuracy of relative sensitivity factor, correction for electron transmission function, surface volume homogeneity, correction to energy dependent electron mean free path, and the degree of sample degradation due to analysis. Under routine work conditions, where the surface is a mixture of contamination and expected material, the accuracy ranges from 80~90% of the value reported in atom % values. The detection limits are 0.1~1.0 atom % (0.1 atom % = 1 part per thousand = 1000 ppm), depending on the detection sensitivities of the specific element. By extending the analysis time, an ultimate detection limit of

approximately 100 ppm for most elements can be achieved.

When using the XPS technique to characterize nanomaterials, it should be noted that the analysis area (minimum: 10~200 μm) is much larger than single nanostructures, thus the obtained composition information reveals average values. On the other hand, the limit in detection depth (1~10 nm) should also be considered. The homogeneity of the nanostructures can strongly affect the accuracy of XPS detection.

§ 2.2.6 X-ray Diffraction

Since the wavelength of X-ray (0.01~10 nm) is comparable to the distance between atoms in molecules, X-ray diffraction (XRD) can be used to characterize the molecular and atomic structures of the sample materials, especially the periodic ones like crystals. XRD is a non-destructive analytical strategy which reveals information about the crystallographic structure, chemical composition, and physical properties.^[83]

XRD reveals the geometry of a molecule based on the elastic scattering of X-ray in ordered structures. The most comprehensive description of X-ray scattering in crystals is given by the dynamical theory of diffraction. As shown in Figure 2-10(b), coherent X-rays are elastically scattered by two parallel atomic planes, inducing phase difference in the reflected rays due to different paths. Constructive interference occurs when the phase shift is a multiple of 2π . This condition can be expressed by Bragg's law:

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

where n is an integer determined by the order given, 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

Figure 2-10 (a) Photograph of a Bruker D8 Advanced X-ray powder diffractometer. (b) Schematic illustration showing X-rays interact with crystalline lattice.

and the scattering planes. Thus the plane spacing is $d = n\lambda/2 \sin \theta$ ($n = 1$ is applied to most of the peaks in real XRD patterns).

Various XRD techniques are developed for specific materials and applications. Powder XRD is able to characterize the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples. It is a simple version of XRD where the X-ray generator and the detector can only rotate along one orientation. Powder XRD is widely used to identify unknown substances, by comparing the acquired pattern to a database maintained by the International Centre for Diffraction Data. It is also adopted to investigate heterogeneous solid mixtures to determine relative abundance of crystalline compounds and, when coupled with lattice refinement techniques, provide structural information on unknown materials. On the other hand, crystals with small grains show broadened peaks in XRD patterns and the accurate grain size can be calculated using the Scherrer Equation:

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$

where K is the shape factor, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity in radians, and θ is the Bragg angle. τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size. The dimensionless shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite.

High-resolution XRD is the advanced version of the diffractometer. It is designed that the measuring vector (along angle bisector between the generator and the detector) can point to any position according from the sample. The diffracting strength reflects the structure of the reciprocal space of the sample. High-resolution XRD is used to investigate thickness, crystallographic structure, and strain in single crystal or textured samples. In theory, high-resolution XRD can be used to map the whole three dimensional reciprocal space of the sample, thus retrieving full information of its structure in real space. However, 3D reciprocal space scanning will take too much time, thus not feasible. In practice, we can choose to scan along a 1D track (e.g., θ - 2θ scan and Φ scan) or map in a 2D area (e.g., pole figure mode and reciprocal space mapping) to obtain structural information of the sample from different aspects.

Chapter 3

Fabrication of ZnO and SnO₂ Semiconductor Nanowires: Growth Mechanisms and Doping Effects

§ 3.1 Introduction

§ 3.1.1 ZnO and SnO₂: Wide Bandgap Semiconductors

ZnO and SnO₂ nanomaterials have drawn a lot of interests due to their importance as wide bandgap semiconductors. At room temperature, bulk ZnO and SnO₂ show direct

Figure 3-1 Typical transistor behavior of (a) ZnO NW and (b) SnO₂ NW.^[86-87] Inset in

(b) illustrates a typical structure of the transistor with NW as channel.

bandgap of 3.37 eV and 3.62 eV, respectively.^[84] They are transparent in visible light and sensitive to UV photons. Tuning bandgap is important for the emission applications. The bandgap of ZnO can be adjusted around 3.0~4.0 eV by Cd or Mg doping.^[85] Although GaN/InN/AlN system is the mainstream and covers much of the same emission range, ZnO shows some advantages. For example, the exciton binding energy of ZnO (~60 meV) is larger than GaN (~25 meV), and may induce higher light emission efficiency.

Pure ZnO and SnO₂ are *n*-type semiconductors due to oxygen vacancies. Transistors with good performance were fabricated using ZnO and SnO₂ nanowires (NWs) as channel materials,^[86-90] as shown in Figure 3-1. Since ZnO and SnO₂ are wide bandgap semiconductors, these transistor-structured devices are also sensitive to corresponding UV wavelength and could be used as UV photodetectors.^[91] Compared to bulk materials, the surface to volume ratio of NWs are much larger. Thus the surface states and the ambient

Figure 3-2 SnO₂ NW gas sensor with Ag NP surface decoration.^[96] (a) The current response of this sensor to ethylene flow at various temperatures. Inset: the magnified curve at 130 °C. (b) TEM image of a SnO₂ NW decorated with Ag NPs. The scale bar indicates 200 nm.

may strongly affect the carrier density and mobility of semiconductor NWs. Previous reports confirm that both ZnO and SnO₂ NWs show potential applications as gas sensors.^[92-94] It was proposed that decorating the surfaces of semiconductor NWs with suitable catalyst nanoparticles (NPs) could enhance the sensitivity of the NW gas sensors.^[95] For example, the sensitivity of SnO₂ NWs to ethylene is increased when the NW surfaces are decorated with Ag NPs (see Figure 3-2).^[96] Moreover, ZnO and SnO₂ NWs have found applications as solar cells,^[97] photocatalysts,^[98] field emission electron sources,^[18] and so forth.

ZnO NWs are also popular due to their unique properties and applications. For example, ZnO is piezoelectric material and electrical signals can be generated by bending

Figure 3-3 ZnO NW nanogenerator proposed by Wang *et al.*^[99] (a) Schematic illustrates the design and structure of the nanogenerator. (b, c) The mechanism of the generator driven by an ultrasonic wave.

or pressing ZnO NWs. As shown in Figure 3-3, Wang *et al.* proposed a nanogenerator using ZnO NW arrays.^[99] ZnO NW may also be used in self-sustain nanodevices in future. In another example, nanolasers were fabricated using well-structured hexagonal ZnO NWs as resonant cavities.^[100]

§ 3.1.2 Nanowire Synthesis: VLS and VS Mechanisms

Nanostructured ZnO and SnO₂ materials can be easily fabricated due to their anisotropic crystal structures. Previous reports tested various synthesis methods, such as vapor transport,^[100-102] hydrothermal,^[103-104] pulsed laser deposition,^[105-107] molten salt,^[108-110] and plasma treatment.^[111] However, precise control on the sizes and morphologies of these nanomaterials is still challenging.

In the widely adopted vapor transport method, vapor–liquid–solid (VLS) and vapor–solid (VS) mechanisms may occur simultaneously and compete with each other. VLS was first discovered by Wagner *et al.* in the growth of silicon whiskers.^[112] In the VLS growth, it is important to choose an appropriate catalyst and synthesis temperature so that there is a coexistence of liquid alloy and solid NW material.^[113] The source material is evaporated first, and then forms a eutectic liquid alloy with the catalytic NPs. The ensuing supersaturation leads to the precipitation and the growth of NWs at the interface between the substrate and the liquid NPs. The catalytic particles (or droplets) normally stay at the growth front, i.e., at the top of the NWs.

On the other hand, it is also frequently observed that NWs can be synthesized without the application of catalyst droplets during the growth,^[114-117] following the

vapor–solid (VS) growth mechanism.^[118-119] Such an anisotropic growth could be the result of several factors such as different growth rates of different crystal orientations (possibly from the difference in surface energies and so forth), existence of dislocations, or preferential accumulation of impurities on certain facets. For ZnO, the growth speed is crystallographic-direction dependent, with the [001] direction much faster than [100] and [210]. Due to the constraints that originated from liquid-phase catalyst NPs, beyond one dimensional NWs and nanorods, the VLS process seldom leads to the formation of complex structures. In general, the VS mechanism is the driving force behind the synthesis of many kinds of ZnO architectures and hierarchical nanostructures, such as tetrapods,^[120] nanotubes,^[121-122] nanoneedles,^[123] nanohelices and nanosprings,^[124] nanorings,^[125] nanodisks,^[121, 126] nanodonuts,^[127] nanobridges and nanonails,^[128] nanopins,^[129] nanocombs,^[130] nanowalls,^[131] nanoflowers, and so on.^[132-133]

Under a certain environmental condition it could be controversial how VLS and VS mechanisms compete with each and what roles the catalytic particles play in the growth process. In the second part of this chapter, we report a systematic study on ZnO NW growth by tuning two important parameters: Zn vapor pressure and catalyst. Catalyst metal selection is of vital importance to achieve the desired NW morphology and to avoid any potential detrimental contamination.^[134] Recently, 15 metal catalysts of periods IV, V, and VI were used to grow SnO₂ NWs, and their performances were compared.^[134] For the growth of ZnO NWs, besides Au, there are also reports using Sn, Ni, Cu, and Se as the catalysts.^[129, 135-138] We purposefully chose Au, Pt, and Ag because they are physically active, but chemically inert. We found that both Pt and Au remain inert at all temperatures used in our experiments, while Ag oxidizes quickly above 500 °C. The state of the NPs is

of vital importance in determining the growth mechanisms, since the existence of liquid metal droplets is a prerequisite for the VLS process to occur. Indeed, liquid-state Au and Pt NPs lead to the VLS growth of ZnO NWs at 800 °C. However, we found that at 500 °C the VS process plays a dominating role even when the liquid-phase catalytic NPs are present. In general, there exists a dynamic competition between the VLS and the VS mechanisms, and the winner is determined by subtle changes of experimental conditions.

§ 3.1.3 Doping Effect

Although most early works concentrated on pure ZnO and SnO₂ nanostructures, recently more and more efforts are devoted to investigate their doped counterparts.^[139-145] For semiconductors, doping is a powerful tool to tailor their electrical and optical properties, facilitating the construction of various electronic and optoelectronic devices. For example, Cu doping could modify the photoluminescent (PL) transitions in ZnO by creating localized impurity levels.^[146] Additionally, Cu may behave as acceptor in ZnO with energy level locating at 0.17 eV below the bottom of the conduction band, making itself a good candidate for producing *p*-type ZnO.^[147] More interestingly, previous studies, both theoretical and experimental, showed that ZnO doped with appropriate transition metal elements perform as diluted magnetic semiconductors (DMS),^[84, 148] which attracted a lot of interest due to their potential applications in spintronics.^[149] In the third part of this chapter, we discuss an interesting discovery that Cu-doped ZnO by vapor transport method with mixed Zn and CuCl₂ powder as the source material shows strong

effect of structure modification, exhibiting a continuous morphological evolution from nanoneedles to nanonails.

Similar phenomenon is also observed in the Ti doped SnO_2 nanostructures. In the growth of 1D SnO_2 nanomaterials, dramatic morphology changes from NW to nanobelt (NB) can be induced by adding TiO_2 to the source powder (SnO_2 + graphite). We investigated the vapor transport growth of SnO_2 in detail and compared the impact of various growth parameters. Adding TiO_2 into the source powder gives us an additional degree of freedom to achieve the selective growth of SnO_2 NBs and NWs. Although the Ti doping level is very low and cannot be determined by the experimental techniques accessible to us, the surface-orientation-dependent energy modification appears to be the origin of the morphology change. Furthermore, the lateral sizes of both NWs and NBs could be tailored in wide ranges by adjusting the various experiment parameters. Finally, as a consequence of their different morphologies, SnO_2 NWs and NBs show different optical and field emission properties.

§ 3.2 Mechanism Control in ZnO Nanowire Growth by Selecting Catalysts and Substrate Temperatures

§ 3.2.1 Experiment

ZnO NWs were synthesized by the conventional vapor transport method (see §2.1.2). ZnO/graphite (weight ratio 1:1) or Zn powder was used as the source material. A small one-end-open quartz tube with a diameter of 1 cm containing the source was put near the middle of the tube furnace. Si substrates pre-sputtered with 3 nm Au, Pt, or Ag

films were placed a few centimeters downstream. The growth temperature (source position) was 1100 °C and 500 °C for ZnO/graphite and Zn source, respectively. The substrate temperature was measured to be ~800 °C and ~500 °C, respectively. During the growth, Ar with a trace amount (0.05%) of O₂ was supplied (100 sccm) as the carrying gas. The as-grown NWs were characterized by SEM, TEM, EDS and XRD techniques.

§ 3.2.2 Result and Discussion

Figure 3-4 shows top and perspective views of the as-grown NWs, whose diameters are 46.5 ± 11.7 , 111.9 ± 52.0 , and 90.3 ± 36.1 nm for the Au, Pt, and Ag cases, respectively. Au NPs result in the thinnest and longest NWs. In order to obtain some information on the growth speed, we terminated the growth immediately after ramping to the highest temperature and found that the nanowires are already 0.4 µm long. The average nanowire length is 0.6 and 1.5 µm after growth time of 1 and 3 min, respectively.

Figure 3-4 SEM top and perspective views of NWs grown from a ZnO/graphite source at 800 °C on (a) Au, (b) Pt, and (c) Ag NPs. Their histograms of size distribution are shown on the right side.

Figure 3-5 XRD patterns of three NW samples grown on Au, Pt, and Ag NPs, respectively.

Therefore the growth speed is approximately 10 nm/s at the initial stage of growth and then decreases as the source powder runs out. NWs grown on Ag catalyst film are much shorter than the other two cases. For all samples, XRD peaks related to ZnO shown in Figure 3-5 can be indexed as the wurtzite structure ($a = 3.25 \text{ \AA}$ and $c = 5.21 \text{ \AA}$). Only Au and Pt peaks are identified in the XRD data, indicating that they remain inert during annealing, consistent with previous studies.^[150] However, we found that Ag forms compounds of Ag_4SiO_4 and AgO .

In control experiments we patterned the metal films before annealing and found that NWs grow only in areas coated with NPs, not on a bare Si surface. Although catalytic NPs are of vital importance for the growth of a wide range of nanowires, their state and kinetics remain controversial.^[151] To study the morphological evolution of the NPs and their roles in the NP growth, 4 nm sputtered films of Au, Pt, and Ag are annealed at different temperatures for 30 min without NW growth. In all three cases, liquid-droplet-like NPs emerge at temperatures well below their bulk melting points,

Figure 3-6 SEM images of (a) Au, (b) Pt, and (c) Ag NPs annealed at different temperatures. Histograms of size distribution for Au at annealing temperature from 500 to 800 °C, for Pt at 700 °C, and for Ag at 500 °C are shown on the right side.

which are 1064, 1772, and 962 °C for Au, Pt, and Ag, respectively. Such significant size-dependent reductions of melting points have been reported to be in excess of that predicted by the Gibbs-Thompson theory.^[152] As shown in Figure 3-6, the Au film forms NPs with homogeneous size distributions at all annealing temperatures, concurring with the prevalent usage of Au as catalyst for NW growth. The NP diameters are 14.7 ± 3.9 , 14.8 ± 3.6 , 13.7 ± 3.3 , and 10.6 ± 4.2 nm at 500, 600, 700, and 800 °C, respectively. The smaller particle sizes at 700 and 800 °C could be a result of their more spherical shapes at these higher temperatures. At 500 °C the Pt film does not form NPs, but shows very fine cracks instead. Particles with irregular shapes emerge at 600 °C as a result of enhanced but still limited mobility. Circular Pt particles with a diameter of 18.7 ± 8.4 nm eventually form at 700 °C. Ag forms circular particles at 500 °C with a size distribution of 38.4 ± 18.5 nm, much larger than the previous two cases, suggesting stronger agglomeration. Oxidation of Ag NPs starts and accelerates at 600 and 700 °C, reflected by the strong

Figure 3-7 TEM images of ZnO NWs grown from ZnO/graphite source at 800 °C on (a, b) Au, (c) Pt, and (d) Ag NPs.

charging effect in the SEM images, which is consistent with the XRD results. Ag NPs after oxidation do not change much in size and shape as annealing temperature increases, suggesting that they are in the solid phase. As shown in Figure 3-4, ZnO NWs grow at ~800 °C in all three cases including Ag. Therefore, we can conclude that liquid droplets are not a prerequisite for the NW growth, although Figure 3-4 suggests that liquid nanodroplets (Au and Pt) result in NWs with a better quality, i.e., longer and more uniform, than the solid counterpart (Ag).

TEM data in Figure 3-7 show that for the Ag and Au cases there is no metal or alloy NP on the ends of the NWs. It is not surprising for Ag because it is already oxidized into solid particles before the NW growth starts. However, for Au, several groups observed terminating Au catalytic NPs, which is generally considered as an indicator for the VLS growth.^[130, 153-154] The absence of NPs in our case could be a result of enhanced evaporation or migration of Au under the particular environmental conditions used in our experiments. Recently, some studies have suggested that the NW growth process is much more complex than the conventional VLS picture. A recent TEM study showed that Au exhibits high mobility and can migrate along the Si NWs.^[155] The depletion of Au from the growth fronts, i.e., the NW tops, eventually terminates the NW growth. Another study

showed that Au resides around the base of ZnO NWs instead of at the top.^[156] It was claimed that the VS mechanism controls the NW growth although the VLS mechanism is responsible for the formation of [001]-oriented ZnO nuclei at the initial stage. However, for two reasons, we believe that VLS still is the dominating mechanism for the growth at 800 °C with Au and Pt catalysts. First, for the Pt case we observed multiple tiny NPs at the NW ends, highlighted by arrows in Figure 3-7(c) and identified as Pt by EDS. It corroborates the scenario that the NPs remain in liquid form with high mobility and migrate or evaporate away from the NWs during the growth process, similar to previous studies.^[138, 155] Such an annihilation effect could be weaker and slower in the Pt case than in the Au case, leaving tiny Pt NPs. Second, a high vapor pressure is required for the VS mechanism to occur. The Zn vapor from the ZnO/graphite powder source is much less than from the Zn powder source. The large diameter of the furnace tube further reduces the effective supersaturation of Zn vapor. Under such experimental conditions the VS process could only result in NWs with much lower quality, namely, shorter length and inhomogeneous diameter distribution. That is the case for Ag, where VS is the only mechanism due to the absence of liquid-state catalyst. Therefore, for the cases of Au and Pt, we believe that the VLS mechanism plays a very important role although the VS mechanism might take over after the metal NPs are depleted from the growth fronts.

Since Pt does not form NPs at 500 °C, we can assess the importance of NP morphology for the NW growth by conducting experiments at this particular temperature. Both Zn powder (source material) and Si substrates are heated to 500 °C with other experimental conditions kept the same. As shown in Figure 3-8, thick NWs with flat hexagonal tops are grown for all three cases. For the case of Ag, ZnO NWs grow much

better at 500 °C than at 800 °C, which could be a result of less oxidation. Since Pt nanoparticles do not form at 500 °C, from Figure 3-8(b) we can conclude that NP morphology is not a prerequisite for NW growth. On the other hand, the nanoscale cracks in the 500 °C annealed Pt film shown in Figure 3-6(b) serve as nucleation sites for the Zn vapor absorption. As shown in Figure 3-8(d), NWs do not grow on bare Si substrates, but on some defective structures such as scratches. Certainly the nanoscale regular cracks on the 500 °C annealed Pt films provide much better nucleation sites for the NW growth, leading to high-density growth and homogeneous size distribution. Similarly, high-quality ZnO NWs were previously grown on other surfaces with microcurvatures such as carbon cloth.^[157] We also note that at 500 °C Pt does not form liquid droplets with Zn vapor. Otherwise, alloy particles similar to the 800 °C case would have been observed at the ends of NWs due to the lower mobility of Pt atoms at 500 °C. Since no liquid phase NP is involved in the Pt case, the NW growth has to follow the VS route.

At 500 °C, Au and Ag already form liquid-phase droplets and start trapping Zn vapor with high accommodation efficiency. However, we argue that the VS mechanism still plays a much more important role than the VLS mechanism on the basis of the following two observations. First, compared with the 800 °C growth, evaporation and migration of

Figure 3-8 SEM images of ZnO nanowires grown from a Zn source at 500 °C on (a) Au, (b) Pt, and (c) Ag. (d) Sparse nanowires grow around scratches on a bare silicon substrate.

catalysts should be much weaker due to the lower temperature. The fact that all the NWs show smooth flat hexagonal tops regardless of catalyst types suggests that the VLS mechanism cannot play the dominating role in this low-temperature growth. Otherwise we should have seen the remains of catalysts at the end of NWs. The well-defined hexagonal column shape of the NWs also suggests the anisotropic growth and the VS mechanism. Second, in this set of experiments the supersaturation pressure of the Zn vapor is much higher than the previous one, which may affect the competition between VLS and VS growth. The impingement rate on the NW ends, W , is given by

$$W = \pi r^2 p \sqrt{\frac{m}{2\pi kT}}$$

where r is the NW radius, p is the Zn vapor pressure, m is the mass of the Zn atom, k is the molecular gas constant, and T is the absolute temperature of the vapor phase.^[118]

Therefore, a higher vapor pressure increases the growth rate and promotes the VS growth. The Zn powder source produces a much higher vapor pressure than the ZnO/graphite powder source. In our experiments, we routinely observed that the pressure inside the furnace tube rapidly increases after the Zn source is heated to 450 °C. On the other hand, we did not notice such dramatic variations of pressure when using the ZnO/graphite powder source. Although in the Au and Ag cases, the strong nonequilibrium conditions may even trigger both VLS and VS growth simultaneously,^[156] the high vapor pressure associated with the Zn powder source may favor the VS mechanism in general. When we increased the growth temperature higher than 500 °C, nanocombs frequently appeared, suggesting a more violent VS growth. Certainly, further studies are imperative to assess the individual contributions from the VLS and VS mechanisms if other experimental variables, such as gas flow rate, gas pressure inside the furnace tube, source temperature,

and so forth are changed.

In general, compared with the VS mechanism, the VLS mechanism enforces much more strict requirements on the experimental conditions and the catalysts used. In our experiments the liquid-state NPs of Au and Ag at 500 °C did not lead to the VLS growth, likely due to the low mobility of Au and Ag atoms. The Zn vapor may not form alloys with Au and Ag or condense out near the substrate to form ZnO NWs with oxygen. In other words, Au and Ag NPs merely serve as nucleation sites, trapping Zn vapor, similar to the role played by the Pt film with nanocracks. A recent study on InAs nanowire growth also suggested that the VLS mechanism does not apply and Au particles merely provide a low-energy interface to collect precursor materials.^[158] Compared with conventional VLS processes, ZnO NW growth is unique due to the existence of oxide in addition to metals and alloys. Furthermore, with the exception of the Sn–Zn and In–Zn combinations, the phase diagrams of Zn alloying with many metals are much more complex than those involving conventional semiconductors.^[113] The V-shaped phase diagrams of Au–Si, Fe–Si, and Au–GaAs have been used to predict the formation of NW within certain ranges of temperature, which were verified by experiments. However, the absence of a pronounced V-shape in most phase diagrams of Zn alloys indicates a different growth mechanism. Therefore, the oxide formation must play a critical role and requires further fundamental studies. Compared with non-oxide semiconductors, ZnO NW growth appears to be more subtle and many details remain unclear.

Recently, several groups have reported on a self-catalyzed growth,^[159-160] namely, Zn liquid droplets condensing and acting as a catalyst for the ensuing NW growth. Such self-catalyzed growth involves liquid droplets, but not external catalysts. Therefore, it is

different from the conventional VLS growth. In many aspects, such a self catalyzed growth resembles the VS process except the existence of liquid Zn droplets at the NW ends during the growth. However, this mechanism may not be dominant in our case. In the self-catalyzed mechanism, sharp tips were found at the ends of NWs as a result of condensation from a liquid phase.^[160] However, in our experiments, all the NWs grown at 500 °C show smooth flat tops. Furthermore, the self-catalyzed mechanism enables growth on bare Si substrates.^[160] On the contrary, we saw few NWs on bare substrates or areas not covered by catalysts. Therefore, although the substrate temperature (500 °C) is higher than the melting temperature of Zn (419 °C), upon absorption Zn vapor immediately forms ZnO with oxygen and no liquid Zn droplet is formed.

§ 3.2.3 Summary

Table 3-1 summarizes the experimental conditions we used as well as the proposed growth mechanisms for each case. We found that the Zn powder source produces a very

Table 3-1 Summary of Experimental Conditions, Catalyst States, and Growth Mechanisms of NWs

	source					
	mixed ZnO/graphite powder			Zn powder		
substrate temperature	800 °C	800 °C	800 °C	500 °C	500 °C	500 °C
Zn vapor pressure	low	low	low	high	high	high
catalyst material	Au	Pt	Ag	Au	Pt	Ag
state of catalyst	liquid	liquid	solid	liquid	solid	liquid
growth mechanism	VLS	VLS	VS	VS	VS	VS

high vapor pressure, facilitating the VS growth regardless of what catalytic particles are used. The thinnest and longest NWs are grown on Au, facilitated by the homogeneous NPs formed in a wide range of temperatures. Ag NPs are effective for growing NWs at 500 °C. But at higher temperatures Ag oxidizes quickly, resulting in low-quality NWs. The Pt film forms cracks at 500 °C, but NWs can still grow via the VS mechanism.

The presence of catalytic NPs is critical for NW growth although neither liquid-phase droplets nor NP morphology is a prerequisite. In our control experiments, very few NWs grow on smooth bare Si substrates no matter what source or catalyst we used. Selecting catalytical NPs and source materials appears to be an effective approach to adjust the competition between the VLS and the VS mechanisms and to tailor the growth of ZnO NWs with desired morphologies and properties. For the VLS process, nanoscale liquid droplets are indispensable due to their ability to effectively absorb and form alloys with Zn vapor. On the other hand, for the VS growth, which dominates in most situations, these NPs mainly provide nanoscale nucleation sites. High-quality ZnO NWs should grow with many other catalysts under the conditions that these catalysts form NPs with a homogeneous size distribution and that they do not oxidize under the growth environment. More detailed investigations related to catalysts are imperative to grow NWs with controlled morphology and to dope NWs with active elements to achieve desired functionalities. The methodology elaborated here should be applicable to these future endeavors on NW growth.

§ 3.3 Cu-Doping Induced Morphology Evolution of ZnO Nanostructures

§ 3.3.1 Experiment

As shown in Figure 3-9(a), the experimental setup is similar to the growth of pure ZnO NWs. Zn (0.5 g) and CuCl₂ (0.1 g, melting point: 620 °C) mix powders were ground for 30 min and used as source materials. They were then inserted into the bottom of a slender one-end-sealed quartz tube (ϕ 10 mm). The aim of this slender quartz tube is to concentrate the source vapor, which is critical for the formation of nanoneedles and nanonails. It was put into the center area of a horizontal tube furnace (Lindberg/Blue M) with the opening facing right (downstream direction according to the carrying gas). Si substrates were placed a few centimeters from the source on the right side, both inside and outside of the slender tube. As we will show later, the location of the substrate appears to be an important factor determining the morphologies of the final products. 2 nm Au films were used as the catalyst and were predeposited on the substrates by sputtering. Ar + O₂ (5%) was used as the carrying gas and blew from left to right at a flow rate of 50 sccm. The pressure was maintained at 20 mbar inside the furnace tube. Typically, the temperature was raised to 650 °C with a ramping rate of 50 °C/min and cooled down quickly to room temperature after 15 min of growth. Pure ZnO NW samples were fabricated through the same route (no CuCl₂ is used) for comparison. The as-fabricated Cu-doped samples show a light pink or red shade in addition to the dark gray color of the pure ZnO NW sample.

The samples were further characterized by XRD, SEM, TEM, EDS and XPS

techniques. PL was studied at room temperature by using a continuous-wave He–Cd laser with a 325 nm line. Magnetization measurements were carried out using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMSXL-5).

Figure 3-9 (a) A schematic drawing of the experimental setup. (b) SEM image of pure ZnO NWs grown without CuCl_2 in the source. (c–g) SEM top views of Cu-doped ZnO nanostructures. The insets show the closer views. The five images are the same in size. (h) The dependence of the cap diameter of nanonails on the distance from the left edge of the substrate. The inset is a photograph of an actual sample with a dimension of $\sim 8 \times 5$ mm. The locations of the SEM observations are highlighted.

§ 3.3.2 Result and Discussion

Without CuCl_2 in the source, under the same experimental conditions, the pure ZnO samples always show the commonly reported NW morphology (Figure 3-9(b)). On the other hand, the morphology of Cu-doped ZnO nanostructures exhibits a sensitive dependence on the locations of the substrates. Nanoneedles were always found on the substrates located inside of the slender quartz tube (position 1 in Figure 3-9(a)), while nanonails often grow on the substrates put right outside of the tube (position 3 in Figure 3-9(a)). A gradual transition between these two morphologies was sometimes observed on the substrate put purposely on the rim of the slender tube (position 2 in Figure 3-9(a)). Figure 3-9(c–g) show typical SEM images of the Cu-doped ZnO nanostructures with a continuous evolution from nanoneedles to nanonails. The locations of the SEM observations are depicted on the photograph of the actual sample as shown in the inset of Figure 3-9(h). Figure 3-9(h) plots the cap sizes of the nanonails as a function of the distance from the left edge of the sample, which exhibits a monotonic increase. The diameter of the hexagonal caps can go from tens of nanometers up to several micrometers, while the sizes of conelike “body” and thin “neck” remain roughly unchanged. When the size of the nanonail caps increases beyond 5 μm , there is significant overlapping between the caps. In this situation, continuous films are formed with porous structures underneath due to the much smaller dimensions of the necks. It is generally believed that the formation mechanisms of nanonails and nanoneedles are very different due to their dramatically different morphologies. However, herein we demonstrated that a continuous transition from nanoneedles to nanonails can be reliably produced on a substrate with a size of only a few millimeters (the inset of Figure 3-9(h)). The morphologies of the

nanostructures are unambiguously determined by the selection of source powder and the location of growth substrate.

In Figure 3-10, the TEM images of nanoneedles were taken on the samples shown in Figure 3-9(c). The low resolution image (Figure 3-10(a)) indicates that the nanoneedles are connected at their bases. As shown in Figure 3-10(b), the typical dimension of the small needles on top of the cones is ~ 100 nm. The HRTEM image (Figure 3-10(c)) indicates that the growth direction is $[0001]$ with a coherent transition between the cone and the neck. The absence of visible defects, second phase, or precipitation means that the dopants are well-integrated into the lattice sites. The SAED pattern (Figure 3-10(d)) is consistent with the hexagonal wurtzite structure of ZnO with no second phase detected. Therefore, we can conclude that the Cu doping does not perturb significantly the lattice

Figure 3-11 (a, b) TEM images of nanoneedles, A HRTEM image (c) and SAED pattern (d) were taken at the area specified in (b).

Figure 3-10 (a, b) TEM images of two nanonails. A HRTEM image (c) and SAED pattern (d) were taken at the area specified in (a)

structure of the ZnO matrix.

The crystalline structure of nanonails was also studied by TEM. The low resolution TEM images of parts (a) and (b) of Figure 3-11 were taken on the samples shown in parts (d) and (f) of Figure 3-9, respectively. The top surfaces for both samples appear to be quite flat, consistent with the SEM observations. The roughness increases significantly in the neck and the cone areas underneath. Although the cap of the nanonails can reach several micrometers, the necks have much smaller dimensions of a few hundreds of nanometers. The HRTEM image (Figure 3-11(c)) taken on the nanonail sample indicates that the growth direction is along [0001], the same as the nanoneedles. The SAED pattern (Figure 3-11(d)) of nanonails shows a good crystalline nature and is consistent with the HRTEM image.

XRD was used to study the crystal structures and the results are shown in Figure 3-12(a). Only ZnO peaks were found in all the samples. Both the nanoneedles and the nanonails have the wurtzite structure. The absence of Cu, CuO, or Cu₂O peak excludes the existence of Cu-based clusters within the detection limit. The high intensity of the (002) peak suggests that [0001] is the preferred growth direction. As shown in Figure 3-12(b), the (002) peaks of the doped sample show a clear shift of $\sim 0.04^\circ$ to the right compared to the pure ZnO NWs, indicating a smaller lattice constant along *c*-axis, which agrees with previous studies.^[161-162] The shrinkage of lattice constants after doping is due to the substitution of Zn²⁺ (0.06 nm) by smaller Cu²⁺ (0.057 nm).

Figure 3-12 (a) XRD scans of the undoped and Cu-doped ZnO nanostructures. (b) The slow scans of the (002) peaks taken on these two samples.

Figure 3-13 (a) XPS survey spectrum of Cu-doped nanonails. (b) High-resolution scan of Cu 2p_{3/2} and 2p_{1/2} peaks.

EDS data from the nanoneedle sample (not shown) only tells us that the absolute concentration of Cu in the nanostructures is lower than 4%. This value is not accurate due to the unknown contribution from the Cu TEM grid. To determine the precise Cu concentration, we carried out an XPS study on the nanonail sample. In the survey spectrum shown in Figure 3-13(a), a very weak peak was detected at 933.37 eV. Its slow scan in Figure 3-13(b) shows Cu 2p_{3/2} peak at 933.37 eV and Cu 2p_{1/2} at 953.15 eV. The quantitative analysis indicates that the atomic concentrations of Zn, Cu, and O are 52.90, 0.32, and 46.78%, respectively. We found that increasing the CuCl₂ ratio in the source

does not lead to any significant increase of the Cu-doping level, indicating that either the solubility of Cu ions in ZnO is quite low or transporting Cu from the source to the sample is inefficient.^[163-164] Therefore, in this report, we concentrate on the samples grown with 0.1 g of CuCl₂ for the structural, optical, and magnetic characterizations.

It is intriguing which and how the subtle variations of environmental conditions trigger the observed continuous morphological evolution from nanoneedles to nanonails. Controlling morphologies is very important because that the morphology of the nanostructures, as we will show later, strongly affects their luminescence properties. The growth of ZnO nanostructures often invokes not only one mechanism, but a convoluted combination of the VLS and VS processes. Liquid-phase alloy droplets of Au appear to play an important role in the initial stage of growth by absorbing the incoming Zn vapor. Without the Au catalyst, the efficiency of forming nucleation sites on the smooth Si substrates is quite low. However, unlike the conventional VLS growth, the liquid alloy droplets grow into islands with sizes much larger than the initial Au NPs. This is in accordance with the fact that the base areas of the nanoneedles and nanonails show much larger dimensions than the size of Au NPs. In the following stages of growth, the high Zn vapor pressure strongly promotes the VS growth. Therefore, the nanostructure growth in our experiments can be classified as a liquid-phase Au NPs assisted VL process. The dominant fast VS growth often brings about novel self-assembled hierarchical structures, such as nanocombs, and nanobridges.^[165] Indeed, as shown in Figure 3-14, we often observed comb-like structures with parallel nanonail or nanonail side branches (parts (a) and (b) of Figure 3-14), nanobrushes (Figure 3-14(c)), nanochains (Figure 3-14(d)), and nanoflowers (parts (e) and (f) of Figure 3-14).

Figure 3-14 SEM images of self-assembled Cu-doped ZnO nanostructures. Nanocombs with side branches of (a) nanoneedles or (b) nanonails. (c) Nanobrushes with a high density of side branches. (d) A nanochains composed of connected nanonails. Nanoflowers composed of many nanonails with (e) small caps or (f) large caps.

To control the nanostructure morphology, it is very important to understand the factors that determine the growth speeds along various orientations and their relative ratios. The wurtzite structure of ZnO exhibits polar-terminated (0001) and nonpolar low-symmetry ($10\bar{1}0$) faces. It is well known that in most situations the growth rates of the different family of planes follow the sequence $(0001) > (10\bar{1}1) > (10\bar{1}0)$.^[166] There are several reasons why the (0001) plane shows the highest growth speed, promoting the one-dimensional growth. One is that the Zn (0001) plane has the lowest surface energy, which tends to be the most stable to resist oxidation.^[121] Since the temperature of the growth zone is above the Zn melting temperature, this liquid-phase growth front is highly effective to absorb the incoming Zn vapor and maintain a high growth speed. Another factor is that the top areas of NWs always receive a high flux of Zn vapor than the shaft due to the shadow effect intrinsic to all physical vapor

processes.^[128] If the growth along the [0001] direction dominates, then NWs often grow continuously with homogeneous diameters.

However, under certain environmental conditions, other structures like nanoneedles are preferred. In some aspects, the morphological change between NWs and nanoneedles resembles the transition from a layer-to-layer (2D) mode to a three-dimensional (3D) mode in the thin film growth.^[167-168] A flux of vapor particles and surface diffusion of adatoms after adsorption play dominant roles in both processes. In the thin film growth, with negligible surface desorption, the height h describing the local position of the moving surface at $\vec{r}$ obeys a conservation law,^[169]

$$\partial_t h(\vec{r}, t) = -\vec{\nabla} \cdot \vec{j}[\nabla h(\vec{r}, t)] + \eta(\vec{r}, t)$$

where $\vec{j}$ is the surface diffusion current, η represents the fluctuation of the incoming flux. $\vec{j}$ determines the growth morphology and is curtailed by the Ehrlich-Schwoebel barrier (ESB).^[170-171] ESB is a result of the lower atom coordination and the localized nature of the dangling bonds at step edges. During growth, ESB limits the mass diffusion across step edges, which could occur when the atoms move either down from an island or between different facets. The formation of nanoneedles strongly indicates the existence of ESB for the diffusion of adatoms on the ZnO (0001) top surface, that is, the growth front. If ESB is negligibly small and the surface diffusion is not constrained, then the shape of growth products is mainly determined by the crystalline-plane-specific surface energies, and NWs often form as a result. Otherwise, the island nucleation competes against the surface diffusion, preventing the idea layer-by-layer growth on the top surface. The effect of ESB combining with the continuous supply of Zn vapor impinging on the surface basically determines the slop, i.e., the sharpness of the nanoneedles.

In our experiments, the source vapor pressures are among the critical factors determining the size of ESB and the ensuing nanostructure morphologies. The use of CuCl_2 is critical for the formation of nanoneedles and nanonails. Without it, only ZnO NWs can be obtained (Figure 3-9(b)). We note here that, besides CuCl_2 , other rare earth metal chlorides can also trigger the growth of nanoneedles and nanonails. Our preliminary results suggest that nanostructures with similar morphologies can also be grown with mixed Zn and MnCl_2 powder. It is well known that the growth of ZnO nanostructures is very sensitive to the compositional change of the source vapor. For example, several previous reports suggested that a trace amount of In vapor can dramatically increase the evaporation rate and even cause the structural change from [0001] axial NWs to $[11\bar{2}0]$ axial nanobelts.^[128, 172] In our experiments, CuCl_2 decomposes into Cu and Cl_2 vapors, which might selectively modify the growth speeds of various ZnO facets. Similar to the epitaxial thin film growth,^[168, 173] these vapors may also act as surfactants, modifying ESB and the mobility of adatoms. If Cu and Cl_2 absorb preferably on the edge of the growth front, then the subsequent layer grown on top will achieve a slightly smaller dimension, which eventually yields a needlelike morphology.

The SEM and TEM studies indicate that the stems of the nanoneedles and nanonails have very similar conelike morphologies. Therefore, the growth of the hexagonal tops on nanonails must occur at the last stage of the growth process. This scenario is consistent with our proposed model for the nanoneedle growth in the sense that the termination of the Cu and Cl_2 vapors near the end of evaporation changes the mode of growth. The observed nanonails are similar to the undoped products reported previously.^[128, 165, 174] There are at least two factors promoting the formation of nanonails. One is that the top

Figure 3-15 Room-temperature PL spectra of pure ZnO nanowire, Cu-doped ZnO nanonails, and nanoneedles.

surfaces of nanonails always receive more incoming source vapor than the stems underneath due to the shadow effect.^[128] This trend further accelerates as the caps of the nanonails grow bigger. The other factor is the abrupt increase of the O/Zn ratio as the Zn vapor runs out near the end of evaporation. This change may significantly boost the lateral growth along the $[10\bar{1}0]$ direction and promotes the formation of caps on the necks of nanoneedles.^[174] In future, further studies on the effects of environmental factors such as the growth time, the flow rate, the concentration of carrier gas, and the Zn/CuCl₂ ratio are needed to elicit the growth mechanism and to achieve a precise control of the nanostructure morphology.

One natural consequence of the above proposed mechanism is that the nanoneedles should show much higher densities of defects and oxygen vacancies than the nanonails. In agreement with previous reports on ZnO towers,^[175-176] the inset of Figure 3-9(c) shows a high density of defects on the nanoneedle surfaces. In contrast, the top surfaces of nanonails (parts (d–g) of Figure 3-9 and parts (a, b) of Figure 3-10) appear to be very smooth and are free from imperfections. Additionally, the nanonail samples are always located outside of the slender quartz tube and are exposed to a continuous supply of oxygen. The ratio of oxygen/zinc becomes much higher as the source vapor is running out

at the last stage of growth. Therefore, more oxygen is incorporated during the formation of nanonail caps. It is well-known that the densities of defects and oxygen vacancies significantly affect the physical properties of oxide nanostructures. This correlation between structure and property was verified by the PL study. Figure 3-15 shows room temperature PL spectra of the pure ZnO NWs, the Cu-doped ZnO nanoneedles, and nanonails. All the samples show two distinct emission peaks: a sharp one in the UV region and another broad one in the visible green region. The UV peak corresponds to the ZnO band gap, and the green peak is commonly related to singly ionized oxygen vacancies and defects.^[146, 177-178] The UV peaks of undoped ZnO NWs, doped nanonails, and nanoneedles are located at 375.2, 381.9, and 382.3 nm, respectively. This red shift of ~7 nm in the Cu-doped samples indicates a reduction of ZnO band gap caused by the Cu doping. A similar red shift of the UV peak and a band-edge modification were also observed by He *et al.* in Ni-doped ZnO NWs.^[142] This reduction of the band gap with Cu doping also indicates that Cu ions substitute for the Zn sites in ZnO.^[179] Interestingly, the intensity of the UV peak of the nanonail sample is comparable to that of the pure ZnO NW sample, while the nanoneedle sample shows a much lower intensity of the band gap emission than that of the other two samples. The dominance of the green emission in the nanoneedle sample indicates that it exhibits a much higher defect concentration than the nanonails. Since the nanoneedles are just nanonails without caps, we can conclude that the defect distribution in nanonail structures is not homogeneous. There is a much higher concentration of defects on the body surface than on the cap, which is consistent with the SEM and TEM observations.

Recently, there has been intensive interest in studying ZnO-based DMS due to their potential applications in spintronics. However, it is still controversial whether room temperature ferromagnetism (RTFM) observed in these ZnO-based materials is intrinsic or due to the unintentional formation of magnetic metal clusters.^[148] In this sense, studying Cu doping is of vital importance since neither Cu nor Cu-based oxides show strong ferromagnetism. Furthermore, the substitution of Zn by Cu is a *p*-type doping, which may promote RTFM.^[180] Density functional calculations also predicted half-metallic ferromagnetism in Cu-doped ZnO without any clustering tendency of the Cu atoms.^[180] Recently, both RTFM and anomalous Hall effect were observed in Cu-doped ZnO thin films.^[162, 181-182] Heng *et al.* also reported RTFM and magnetic anisotropy in Cu-doped ZnO nanoneedles.^[161] However, there has been no report on the magnetic properties of transition-metal-doped ZnO nanonails. Figure 3-16(a) shows typical *M*-*H* curves of a Cu-doped nanonail sample taken at both 5 and 300 K. The observed hysteresis loops indicate the existence of ferromagnetism at both temperatures, consistent with previous studies.^[161-162, 181] Temperature dependent magnetization (*M*-*T*) curve indicates

Figure 3-16 (a) *M*-*H* loops of a Cu-doped ZnO nanonail sample taken at 5 and 300 K. The inset shows the *M*-*H* loop of the 5 K data in the low-field regime. (b) *M*-*T* data for the same sample.

that the FM transition temperature is higher than room temperature, in accordance with the other reports.^[181-182] The low Cu doping concentration does not favor the conventional super exchange or double exchange mechanism as the origin of the observed RTFM. On the other hand, oxygen vacancies and surface defects could play very important roles in enhancing the magnetism. Our XPS, SEM, and PL data indicate that there are substantial oxygen vacancies and surface defects in the Cu-doped ZnO samples. It has been shown that in clusters of oxygen vacancies, the Hund's coupling energy exceeds the separation between the hybridized orbital levels, giving rise to a net magnetic moment.^[183] Similarly, Durst *et al.* argued that defects tend to form bound magnetic polarons that stabilize the ferromagnetic ordering. The enhancement of RTFM by structural defects has also been observed in transition-metal-doped thin films and nanocrystals.^[184-185] Further studies using SQUID, TEM, and magnetic circular dichroism are needed to determine unambiguously the origin of the observed RTFM.

§ 3.3.3 Summary

Cu-doped ZnO nanoneedles and nanonails were synthesized by thermally evaporating Zn and CuCl₂ powders. We observed a continuous morphological evolution between nanoneedles and nanonails with high tenability and reproducibility. This chloride-based thermal evaporation method appears to be a general approach to fabricate transition-metal-doped ZnO nanomaterials with novel morphologies. Such a controlled doping has extensive implications and affects the crystalline and electronic structures of ZnO. In our experiments, the Cu doping results in a decrease in the lattice parameter and

a red shift of the energy band edge. The strong correlation between morphologies and optical properties was illustrated in the significantly different luminescence properties of nanoneedles and nanonails. Finally, RTFM was detected in Cu-doped ZnO nanostructures, which may find novel applications in spintronics devices.

§ 3.4 Morphology Controlled Growth of SnO₂ NWs and NBs by Ti Doping

§ 3.4.1 Experiment

SnO₂ 1D nanostructures were fabricated by vapor transport method, similar to the growth of ZnO nanostructures discussed above. The growth took place in a horizontal tube furnace equipped with gas supplying and pumping systems. The schematics of two typical experiment setups (i.e., type 1 & 2) are shown in Figure 3-17(a, b), respectively. SnO₂ was mixed with graphite (weight ratio 1:1) and used as source powder (NW growth) after grounding for 30 min. For the NB growth, SnO₂ was mixed with TiO₂ and graphite (weight ratio 1:1:2). The source powder was placed at the end of a quartz test tube

Figure 3-17 Schematic illustration of the experimental setups. (a) Type 1: the quartz tube opens toward the downstream direction. (b) Type 2: the quartz tube opens toward the upstream direction.

(diameter = 1 cm, length = 15 cm). Si (111) substrates (6 × 8 mm) coated with Au film (4 nm) were placed inside the tube near the open end. The quartz tube was then inserted into the tube furnace with the source powder at the furnace center and the open end pointing either downstream (type 1) or upstream (type 2). Ar mixed with O₂ was introduced as carrying gas and the ambient pressure was maintained at 20 mbar. During the growth, the temperature (source position) was ramped to 1100 °C (20 °C/min, substrate temperature: ~800 °C) and maintained for 1 hour. White or light gray products were observed on the substrates.

The morphology, crystalline structure and composition of the products were characterized by SEM, TEM, EDS, XRD and XPS. PL properties were studied at room temperature (RT) using a continuous wave He–Cd laser (325 nm). Raman measurements were performed on a WITEC CRM200 confocal Raman system at RT (excimer: 532 nm). RT field emission (FE) measurements were carried out in a high vacuum (10⁻⁷ mbar) chamber. The distance between the anode and the surface of the emitting sample (cathode) was fixed at 100 μm and the current–voltage (*I–V*) curves were recorded using a Keithley 2400 source meter.

§ 3.4.2 Result and Discussion

SEM and TEM Studies

Our initial intention of using a source of SnO₂ mixed with TiO₂ and graphite was to synthesize nanomaterials based on the isostructural system TiO₂–SnO₂, which may find applications in gas detection.^[186-187] However, as we will show later, the current synthesis method is not effective for doping Ti in SnO₂ due to the very low vapor pressure of Ti. Instead, this synthesis route allowed us to achieve a good morphology control on the SnO₂ nanostructures. Table 3-2 provides a brief summary of the experimental parameters and the results of six typical experiments. SnO₂ mixed with graphite was used as the source powders to prepare samples # 1–3, while TiO₂ was added into the source for the growth of sample # 4–6. The correlations between adding TiO₂ in the source powder and the resulting nanostructure morphologies indicate a simple rule: adding TiO₂ leads to NBs; otherwise NWs form. The existence or absence of TiO₂ dictates the morphologies of the products, though the lateral sizes can be tailored by other growth parameters. No exception was observed in a total of over 50 experimental runs we conducted under different conditions of carrying gas (O₂: 0.05%~100%; flow rate: 30~1000 sccm; pressure: 10~50 mbar), of growth temperature (900~1100 °C), of the experimental setup (quartz tube with both ends open or one end sealed), and even in different tube furnaces

Table 3-2 Comparison of experimental parameters and results.

Sample No.	Tube orientation	Carrying gas		Morphology	Size*
# 1	Type 1	O ₂ (0.05%)	100 sccm	NW	15.3 nm
# 2	Type 2	O ₂ (0.05%)	500 sccm	NW	66.6 nm
# 3	Type 2	O ₂ (5%)	30 sccm	NW	113 nm
# 4	Type 2	O ₂ (5%)	30 sccm	NB	33.6 nm
# 5	Type 2	O ₂ (100%)	200 sccm	NB	114 nm
# 6	Type 2	O ₂ (100%)	1000 sccm	NB	1.7 μm

* Size indicates the average diameter for NWs and the average width for NBs.

Figure 3-18 SEM images of SnO₂ (a–c) NW samples # 1-3 and (d–f) NB samples # 4-6.

Also shown are the corresponding statistical distributions of NW diameter and NB width.

The inset in (b) shows a spherical catalyst droplet on the NW tip. The experimental conditions are listed in Table 3-2.

(Carbolite three-zone or Lindberg/Blue Mini-Mite horizontal tube furnace).

SEM images of NW samples # 1–3 and NB samples # 4–6 are shown in Figure 3-18. The as-synthesized nanostructures are quite uniform in morphology and size. The NWs and NBs are quite long, in the order of tens to hundreds of micrometers. The diameters of the NWs are highly tunable, and a clear incremental trend from sample # 1 to sample # 3 was observed. There are also dramatic increments of NB width from sample # 4 to sample # 6, while the NB thickness remains roughly unchanged and is in the range of 20–50 nm. For each sample, the dimensions of more than 100 NWs or NBs were measured, and the statistical results were plotted in the histograms in Figure 3-18. By Gaussian fitting, the

NW diameters of samples # 1–3 were determined to be 15.3 ± 4.7 , 66.6 ± 38.8 , and 113 ± 74 nm, respectively. The NB widths of samples # 4–6 were estimated to be 36.6 ± 27.1 , 114 ± 100 nm, and 1.7 ± 1.1 μm , respectively. Thus we are able to tune the dimension of the 1D SnO_2 nanomaterials over almost two orders of magnitude.

The oxygen partial pressure appears to be a key parameter: generally, a higher O_2 partial pressure favors the growth of thicker NWs and wider NBs. We can also tell from Table 3-2 that the growth of SnO_2 NBs normally requires a higher oxygen pressure than for growth of NWs. In the SnO_2 NB sample # 6, the width-to-thickness ratio reaches 100, which, to the best of our knowledge, is the highest ever reported for SnO_2 NBs. A substantial fraction of the NBs are wider than 2 μm , which is among the widest belt-like oxide and chalcogenide nanomaterials reported in the literature.^[188-190] The dimensions of most NWs are smaller than the critical value of 90 nm, which is consistent with the calculation by Wang *et al.*^[191] However, the width of the narrowest NBs in sample # 4 also falls into this range, and this contradiction may stem from the surface energy modification induced by Ti.

It is often difficult to determine the exact growth mechanism of 1D nanostructures due to the lack of *in situ* observation. In most cases, there is a competition between VLS and VS mechanisms, and their balance is modified by very subtle changes of growth conditions.^[65] Control experiments showed that no NW or NB would grow on Si substrates without the coating of Au film. However, careful SEM investigations suggest that the growth of SnO_2 NWs and NBs deviates from the conventional VLS mechanism. As shown in the inset in Figure 3-18(b), spherical particles, which were determined to be Sn by EDS analysis, were observed on most of the NW tips, indicating a self-catalytic

VLS dominated growth mechanism.^[192] Such Sn particles were not found on the NBs; thus the growth of NBs is likely dominated by the VS mechanism.

The structures of the as-grown materials were further analyzed by TEM. Low-resolution images are shown in Figure 3-19(a, b). The lacey carbon film under the NBs can be clearly observed, indicating that the NBs are quite thin. The NBs also show smooth side boundaries and uniform thickness. In contrast, the NWs show rough surfaces and their thickness decreases from the centers to the boundaries. The SAED data in the insets indicate that the growth direction of the NBs is $[110]$. The growth of NWs is more complex: the direction is close to $[302]$ with the axial growth plane being (301) . The SAED patterns show no sign of secondary phase and support a pure rutile structure for both NBs and NWs. The HRTEM images of the NB and the NW at the selected areas are shown in Figure 3-19(c, d), respectively. No structural defect was observed, indicating a

Figure 3-19 TEM images of (a) a SnO_2 NB and (b) a SnO_2 NW with the corresponding SAED patterns as insets. (c, d) HRTEM images taken at the marked areas in (a) and (b), respectively. (e) HRTEM image of the NW in (b). The insets show comparisons between the magnified images (upper half) and the simulated patterns (lower half) at three specified positions.

single-crystalline nature. The planes with interplanar d -spacings 0.331 and 0.177 nm can be indexed as $\{110\}$ and $\{211\}$, respectively. The HRTEM results are consistent with the SAED patterns, and confirm the tetragonal rutile structure for both NWs and NBs.

To further study the morphology of the NWs, an HRTEM simulation on rutile SnO_2 was performed using JEMS software with the observation direction along $[11\bar{3}]$. By comparing the simulated images with the experimental HRTEM data, we determined the thickness at a few selected positions on the NW. Similar procedures have previously been used to determine the local thickness of ZnO NBs.^[78] As shown in the insets of Figure 3-19(e), the good matching between the experimental images (upper half) and the simulated ones (lower half) allowed us to determine the local thickness to be 1.2, 14.0, and 23.4 nm at the selected positions. Considering these data along with the NW diameter of ~25 nm, we conclude that the cross section of the NWs is close to a circle. Thus the NW is not a retrogressed NB with the aspect ratio reduced to 1. Otherwise it would show a rectangular or a square-shaped cross section.

XRD and XPS Studies

We carried out additional characterizations on the NW and NB samples. Unless otherwise stated, the NWs and NBs used in the experiments refer to sample # 1 and sample # 6, respectively. Sample # 1 represents the thinnest NWs and sample # 6 the widest NBs. The XRD patterns of the NW and NB samples are shown in Figure 3-20(a). Both of them show tetragonal rutile SnO_2 structure with lattice constants $a = 0.4737$ nm and $c = 0.3186$ nm. The NB pattern shows a higher (110) peak intensity than that of the NWs, consistent with their growth direction of $[110]$ as determined in the TEM

Figure 3-20 (a) XRD patterns of the SnO₂ NWs (sample # 1, upper curve) and the SnO₂ NBs (sample # 6, lower curve). The region marked by a dashed circle is magnified and shown in (b). (c) Detailed scan of the (110) peaks. The result of a control experiment with a higher Ti molar ratio (95%) in the source powder is shown as comparison.

(d) XPS survey spectra of the SnO₂ NWs (sample # 1, upper curve) and the SnO₂ NBs (sample # 6, lower curve). Inset: no Ti_{2p} peak is seen in the high-resolution scans.

observation. As shown in Figure 3-20(b), a weak Sn (200) peak appears only in the NW data. This peak comes from the Sn catalyst droplets on the NW tips, consistent with the SEM observation shown in Figure 3-18(b).

The NW and NB samples show very similar XPS results. As shown in Figure 3-20(d), full range surveys on both NW and NB samples did not detect any peak related to Ti. A detailed scan from 470 to 455 eV also showed no sign of Ti_{2p} peak. Therefore, the Ti doping level is lower than the detection limit of XPS, i.e., 0.1%.

Mechanism of Morphology Control

The salient feature of this study is that adding TiO_2 to the source powder was found to induce significant morphology change in the 1D SnO_2 nanomaterials. In equilibrium or quasiequilibrium growth, the shapes and dimensions of nanostructures are dictated by the differences of surface energies between various growth directions. The surface energies may be influenced by factors such as size effect, supersaturation state, unintentionally introduced impurities, and intentional doping. For example, based on experimental results and theoretical calculations, Wang *et al.* concluded that undoped SnO_2 favors the NW morphology when the size is smaller than 90 nm while the NB morphology is preferred with larger sizes.^[191] Our previous study on Cu-doped ZnO nanostructures showed that a morphology change from NW to nanoneedle and nanonail can be induced by very subtle modifications of the growth environments.

The subtle energy balance between the various growth directions can be broken by minimal changes of composition or environment. It was reported that NWs may change direction during growth to form zigzag-shaped structures because several groups of surfaces of rutile SnO_2 have similar energies.^[193-194] As shown in Figure 3-18, we frequently observed branched NWs. Similar phenomena have also been reported for pure SnO_2 NBs.^[195] However, the growth direction rarely changes in the NB samples, which may indicate that sufficient energy differences are generated between various growth surfaces and the formation of NBs is stabilized.

Herein, we propose that Ti from the source powder modifies the surface energies of SnO_2 , thus particular lateral growth directions are favored, leading to the anisotropic

growth of NBs. Such dramatic changes of growth morphology are similar to the previous observations of conversion between ZnO NWs and NBs by indium doping, which was accounted for by minimization of Gibbs free energy.^[172, 196] However, we should note that Ti may not be doped significantly into SnO₂ matrix even though its decoration on the growth surfaces modifies the surface energy and the morphology. The Ti ions decorating the surfaces may not be incorporated into the bulk effectively, which explains the fact that there is no obvious shift of the (220) peak in the XRD data of NBs shown in Figure 3-20(c).

In our experiments, the vapor pressure of Ti at the growth temperature is quite low (even at 1660 °C it is only 0.49 Pa, and in contrast the vapor pressure of Zn reaches 19.2 Pa at 420 °C), causing the detection of Ti to be extremely difficult. This situation is different from the conventional polycrystal growth through solid state reactions where the structural analogy between TiO₂ and SnO₂ leads to the formation of a solid solution over a wide composition range above the spinodal decomposition temperature.^[187, 197] In order to verify that Ti vapor does come out at the source temperature of 1100 °C, we carried out a control experiment by dramatically increasing the Ti molar content in the source powder. We found that Ti doping becomes much more detectable when the Ti content is high enough although the sample quality is compromised. As an example, Figure 3-20(c) shows a detailed scan around the SnO₂ (110) peak for a case of 95% Ti in the source, which reveals a small peak shift of ~0.1 °, indicating a reduction of the lattice constant by ~0.0015 nm. Since there is a linear relationship between lattice parameters and composition molar ratios in such solid solutions,^[197] it can be calculated that the Ti doping level in the control experiment is ~10%. Therefore, we conclude that Ti vapor does exist

Figure 3-21 (a, b) SnO₂ NWs grown on Ti-coated Si substrates without Au catalyst or with Au catalyst, respectively. (c, d) SnO₂ NWs synthesized with MnO₂ or MgO mixed in the source powders, respectively. (e) ZnO NWs fabricated with TiO₂ powder mixed in the source. (f) Pure ZnO NWs grown without TiO₂ in the source.

under the experimental conditions used although the Ti concentration in the SnO₂ nanomaterials is lower than the detection limits of the XRD and XPS techniques.

To further investigate the effect of Ti doping, we tried to grow SnO₂ nanostructures on Si substrates coated with 10 nm Ti films. The growth parameters were kept the same as in sample # 3. As shown in Figure 3-21(a), with the bare Ti film, the density of SnO₂ NWs is very low. On the other hand, as demonstrated in Figure 3-21(b), dense SnO₂ NWs were grown if a 4 nm layer of Au was sputtered on top of the Ti-coated substrates. Therefore, there seemed to be minimal reaction between the Ti film and the SnO₂ NWs, and doping from the Ti film is not as effective as from the TiO₂-mixed source powder, which may be a result of the lower temperature at the substrate position than the source temperature.

On the other hand, in order to study how general the doping effect is on the morphology, we carried out control experiments with MnO₂ or MgO, instead of TiO₂,

added to the source powder. These two compounds have distinct melting temperatures: MnO_2 decomposes at a low temperature of 535 °C, while MgO has a high melting point of 2832 °C. The same experimental parameters as in the growth of sample # 3 and sample # 4 were used. The SEM images taken on the growth products are shown in Figure 3-21(c) and d. In both cases, SnO_2 NWs with sizes similar to those in sample # 3 were observed, and there was no transition to NBs. The yields were much lower, indicating that the Sn vapor was reduced due to the dilution of Sn in the source.

We also investigated whether adding TiO_2 into the source powder (ZnO + graphite) can induce a similar morphology change in ZnO NW growth. The experimental conditions were similar to those used in a previous report.^[65] As shown in Figure 3-21(e, f), adding TiO_2 into the source powder lowered the NW density and reduced their diameters. Therefore, the morphology change of SnO_2 nanomaterials from NW to NB induced by Ti is not a general effect for other combinations of transition metals and oxides. For a particular nanomaterial, the doping element must be carefully selected in order to induce the surface energy modification and the desired morphology change.

Comparative PL, Raman, and FE Studies

The reliable control of the morphologies of SnO_2 allows us to carry out a systematic and comparative investigation on their physical properties. We compared the PL, Raman and FE characteristics of SnO_2 NWs and NBs because these properties are expected to depend on the morphology. In the RT PL spectra shown in Figure 3-22, a broad peak at ~600 nm (2.06 eV) was observed in both samples. Similar results have been reported before, and this peak was believed to originate from the defect-related electronic states in

Figure 3-22 RT PL spectra of (a) the SnO₂ NWs (sample # 1) and (b) the SnO₂ NBs (sample # 6). Both original data (symbols) and double-peak Gaussian Fittings (lines) are shown.

the band gap.^[198-199] The radioactive interaction between the surface oxygen vacancies and the interfacial Sn vacancies leads to the orange emission. For both NWs and NBs, the broad emission can be well fitted with two Gaussian peaks, possibly suggesting that there exist two different types of radiation center. For the NWs, the two peaks locate at 592.7 and 670.1 nm. For the NBs, they are at 607.3 and 692.5 nm. The emission peaks of the NBs show small red shifts compared to those of the NWs, possibly due to the differences in their morphologies and sizes.^[200]

The RT Raman spectra taken on NW and NB samples are shown in Figure 3-23. Beside the characteristic Raman peak of the Si substrate at 519 cm⁻¹, three fundamental Raman scattering peaks were observed, at 478, 632, and 733 cm⁻¹. These peak positions are in good agreement with the previous results on a bulk crystal of rutile SnO₂ and could be assigned to E_g, A_{1g}, and B_{2g} acoustic vibration modes, respectively.^[201] Compared with the NB sample, the NW Raman scattering shows a dramatic reduction of the A_{1g} peak and

Figure 3-23 RT Raman scattering spectra of the SnO₂ NWs (sample # 1, lower curve) and the SnO₂ NBs (sample # 6, upper curve).

the B_{2g} mode is totally quenched. The size effect may have caused these modifications, and a similar trend was also observed in the Raman spectra of SnO₂ NPs with different sizes.^[202]

Figure 3-24(a, b) show the current density–electric field (J – E) curves in the FE measurements and the corresponding $\ln(J/E^2) - 1/E$ (Fowler–Nordheim, or FN) plots. The turn-on field, defined as the field required to reach a current density of 0.01 mA cm⁻², is ~1.94 and 2.15 V·μm⁻¹ for NWs and NBs, respectively. Compared with NWs, NBs are capable of tolerating a much higher current density; the breakdown current of NBs is more than 30 times higher than that of the NWs. The better stability of NBs is possibly due to their larger cross-section areas and their lower resistance. The FN plots of both samples roughly follow straight lines, indicating that the FE currents can be attributed to the E -field-induced tunneling of electrons from the material surfaces into vacuum through a potential barrier.^[203-204] According to the FN law, the relation between the current density J and the applied field E can be depicted as $J = (A\beta^2 E^2 / \Phi) \exp(-B\Phi^{3/2} / \beta E)$, where Φ is the work function, A and B are constants with values of 1.54×10^{-6} A eV·V⁻² and 6.83×10^9 eV^{-3/2}·V m⁻¹, respectively, and β is the field enhancement factor.

Figure 3-24 (a) Field emission J - E plots of the SnO₂ NWs (sample # 1, square symbols) and the SnO₂ NBs (sample # 6, triangle symbols). The current density of the NWs is multiplied by a factor of 30. (b) Corresponding FN plots.

Assuming that the work function of SnO₂ is 4.5 eV,^[205] we estimated the β values of the NWs and NBs to be 1419 and 2253, respectively. Compared to the previous results,^[199, 206-210] the low turn-on fields and the high β values suggest good FE performances of the synthesized 1D SnO₂ nanomaterials.

§ 3.4.3 Summary

In summary, we have achieved reliable morphology control of SnO₂ NWs and NBs by selectively adding TiO₂ into the source powder during the vapor transport growth. In addition, by adjusting the oxygen content in the carrying gas and the geometry of the experimental setup, we were able to tune the SnO₂ NW diameters from ~15 to ~115 nm

and the NB width from ~ 30 nm to ~ 2 μm . Although the Ti doping level is lower than the detection limits of our experimental tools, we propose the doping-induced surface energy modifications as the origin of the morphology transformation. RT PL, Raman, and FE measurements were carried out on the SnO_2 NWs, and NBs, and the results indicate that the physical properties sensitively depend on their different morphologies. In future, tools with higher sensitivity such as synchrotron-based techniques should be used to unambiguously determine the Ti doping density, which will help to achieve a thorough understanding of the growth mechanism. Furthermore, quantitative theoretical modeling may guide us to select the appropriate doping elements to achieve the desired morphologies for certain host materials. The synthesis strategies reported here may be applied to other material systems to achieve reliable control of the shape and the size of nanomaterials.

Chapter 4

Symmetry-breaking In-plane Synthesis of Self-assembled Si-based Nanostructures: the Magic of Au Nanoparticles

§ 4.1 Introduction

Understanding the silicon/metal interactions and the silicide materials are important for both fundamental sciences and semiconductor technologies. Silicide materials play critical roles in the integrated semiconductor devices, such as CPU. Figure 4-1(a) shows a typical cross section TEM image of a complementary metal-oxide semiconductor (CMOS) device. Source and drain electrodes are constructed by Co silicide in this example. Modern large scale integrated chips such as CPU (Figure 4-1(b)) may contain billions of such components.

Figure 4-1 (a) Fake-colored cross section TEM image of a typical CMOS device (source: IBM). (b) Image of a CPU chip (source: Intel).

Figure 4-2 SEM images of various out-of-plane metal silicide NWs.^[226] All scale bars are 5 μm except Ni_2Si which is 200 μm .

One main objective in studying metal silicides is to search for high-performance interconnects, ohmic contact, and gate materials for electronic circuitry.^[211-213] As the dramatic size shrinking of transistors continues, metal silicide NW of TiSi , CoSi , NiSi , Ni_2Si , TaSi , and PtSi were envisioned to be natural building blocks for semiconductor devices.^[214-226] Recently, a lot of attention is attracted to FeSi , CoSi , $\text{Fe}_{1-x}\text{Co}_x\text{Si}$, and Fe_5Si_3 NWs, due to their potential applications in Si-based spintronic devices.^[48, 227-229] Beside the conventional electronic applications, there are also reports on CrSi_2 NWs

being synthesized and explored as thermoelectric materials for energy generation.^[230-232]

To construct nanoscale silicides, self-assembly is an effective bottom-up approach to overcome the limitations on resolution and throughput of the conventional lithography techniques.^[233-234] Previously, free-standing silicide NWs, as shown in Figure 4-2, were grown by chemical vapor transport from metal halides or single source organometallic precursors.^[48, 220, 225-228, 230-231, 235] Growth of silicide NWs was also achieved by annealing metal or silicide films under controlled ambients.^[221-224]

In addition to free-standing NWs, straight silicide NWs attached to silicon wafers were fabricated based on asymmetric lattice mismatches between the silicides and the host Si substrates. With the Si substrates acting as template, self-assembled epitaxial growths of silicide NWs on Si substrates have been demonstrated.^[214-215, 236-238] Silicide NWs can also grow without anisotropic lattice mismatch, following the “endotaxial” or the strain-driven “shape transition” mechanism.^[239-242] For example, scanning tunneling microscopy (STM) images of ScSi₂, ErSi₂, DySi₂, and GdSi₂ NWs in-plane grown on Si

Figure 4-3 STM topographs (400 nm × 400 nm) showing (a) ScSi₂, (b) ErSi₂, (c) DySi₂, and (d) GdSi₂ NWs in-plane grown on Si (100) substrates.^[243]

(100) substrates are shown in Figure 4-3.^[243]

In this chapter, we studied the fabrication of silicide nanostructures by using the vapor transport method. Cu and Mg related nanosilicide systems were chosen as two typical examples. Cu_3Si and Mg_2SiO_4 nanostructures were synthesized by exposing Si substrates (coated with low density Au NPs) to the corresponding metal vapors at high temperatures. Interestingly, in both cases, self-assembled nanostructures were obtained with morphology dependence on the surface orientation of the Si substrates. That is, by introducing Cu vapor, long-range ordered Cu_3Si nanotriangles (NTs), nanosquares (NSs), and NWs were synthesized on Si (111), (100), and (110) substrates, respectively. When Mg vapor is supplied, Mg_2SiO_4 NWs were formed with specific growth directions (i.e. Si $\langle 110 \rangle$) on all Si surfaces.

Detailed studies revealed that the VLS growth mechanism applies to both systems. However, unlike conventional VLS nanowire growths (such as the synthesis of ZnO and SnO_2 NWs described in last chapter), the fabrication of the silicide-related nanostructures involves the simultaneous reactions between metal vapor, Au catalyst, and substrate. Actually, Si wafers act both as the substrates and the source of Si atoms. As a result of the unconventional endotaxial VLS growth, the morphology of the product nanostructures depends strongly on the substrate surface structures.

Although sharing the similar growth mechanisms, the roles of Au NP catalysts show big difference in these two systems. In the Cu-related system, Au NPs stay still during the growth and help to penetrate the barrier of native oxide layer on Si substrates, thus enabling the growth of Cu_3Si nanostructures. On the other hand, in the Mg-related experiments, the Au droplets float and slide on the substrate surfaces, thus guiding the

growth of Mg_2SiO_4 NWs.

Our study is not only important to the field of silicide nanomaterials, but also contributes to the fundamental understanding of VLS growth mechanism, thus enhancing our abilities to achieve designed fabrication of novel nanomaterials. We have also achieved precise size control of these nanostructures by tuning experiment parameters. As an example of application, Si nanowalls were fabricated by chemical etching using the aligned Mg_2SiO_4 NWs as masks.

§ 4.2 Experiment

These silicide-related nanostructures were fabricated by the vapor transport method. The experiment setup includes a horizontal tube furnace with gas supply and pumping systems. Si (110), (100), and (111) substrates were cut into small pieces (typically 6×8 mm) and cleaned by ultrasonic bath in acetone. No HF treatment was performed and the native oxide layer on the substrates was left intact. In order to distribute Au NPs uniformly, the substrates were treated by oxygen plasma to render hydrophilic surfaces. Au NP suspension (NP size: 5~90 nm) was dispersed on the substrates and dried in air. The density of the NPs was qualitatively controlled by diluting the suspension with deionized water.

In the growth of Cu_3Si nanostructures, mixed powder of CuO and graphite with a total weight of 0.1 g and a weight ratio of 1:1 was used as the source material. CuO was reduced by graphite and generate Cu vapor at high temperatures. Ar was introduced as the carrying gas with a constant flow rate of 50 sccm and the pressure inside the quartz tube

was maintained at 20 mbar. During the growth, the furnace tube was heated for a predetermined period of time to 960 °C (center, source position), and then quickly cooled down to room temperature.

In the Mg-related experiments, Mg_3N_2 powder was placed at the center of the furnace as source material. It decomposed and generated Mg vapor at high temperatures (> 800 °C). The flow of Ar carrying gas was kept at 100 sccm and the pressure in the furnace tube was maintained at predetermined values (around 5~30 mbar). During the growth, the furnace was kept at predetermined temperatures (~900 °C) for a few minutes before being cooled down.

The as-fabricated nanomaterials were characterized by SEM, TEM, AFM, and XRD techniques.

§ 4.3 Morphology and Structure

§ 4.3.1 Cu_3Si Nanotriangle, Nanosquare, and Nanowire

Figure 4-4 shows representative SEM images of the Cu-related samples after growth of 1 min. The substrate orientation and symmetry dictate the shape of the nanostructures. Nanoscale triangles, squares, and wires were observed on Si (111), (100), and (110) substrates, respectively. The equilateral NTs and NSs exhibit lateral dimensions from 140 to 350 nm, and from 240 to 380 nm, respectively. NWs have widths between 190 and 390 nm, and length between 0.6 and 6.2 μm . In a given sample, all the nanostructures have the same orientation. The boundaries of NTs and NSs and the growth direction of the NWs were determined to be along the Si $\langle 110 \rangle$ directions. As depicted in the insets of Figure

Figure 4-4 SEM images of shape-controlled Cu_3Si nanostructures grown at 960 °C for 1 min using 30 nm Au NPs as catalyst. NTs, NSs, and NWs are synthesized on substrates of (a) Si (111), (b) Si (100), and (c) Si (110), respectively. Insets show magnified views of individual nanostructures.

4-4, the corners of the NTs, NSs, and NWs are always rounded, the tops not flat.

30 nm Au NPs were used as catalyst in these experiments. One Au NP can be identified inside the NT shown in Figure 4-4(a). Au NPs were found to be crucial for the growth of Cu_3Si nanostructures; control experiments not using Au NPs did not give any product with regular shape. Careful examinations, however, indicate that only a small portion (~5%) of the Au NPs eventually led to the growth of nanostructures and the process of selective nucleation appears to be subtle.

To characterize the chemical compositions of the nanostructures, XRD studies were carried out. As shown in Figure 4-5(a), the XRD peaks located at 36.5, 42.3, 44.6, and 45.2 °, indicate an $\eta\text{-Cu}_3\text{Si}$ structure for all three samples. Although the XRD peaks are weak due to the low surface coverage of Cu_3Si , they indicate that the nanostructures are at least partially crystalline, not amorphous. The weak peak at 38.3 ° can be assigned to either Au or Cu–Au alloy. According to the Cu–Si binary phase diagram,^[244] $\eta\text{-Cu}_3\text{Si}$

Figure 4-5 (a) XRD data of Cu_3Si nanostructures grown on Si (111), (100), and (110) substrates. The peak marked with star can be assigned to Au or Cu–Au alloy. (b) Schematic illustration of η' - Cu_3Si crystal structure on Si (111).

comprises three phases which appear at different temperature zones and are denoted as η , η' , and η'' . During the cooling process following the high-temperature synthesis, a phase transformation of $\eta \rightarrow \eta' \rightarrow \eta''$ occurs.^[245] η'' is the equilibrium phase at room temperature, and its structure can be considered as a disordered η' superstructure with periodic displacements normal to the η' [111] direction.^[245] Figure 4-5(b) illustrates the crystal structure of η' - Cu_3Si and the atoms in Cu_3Si are located at similar positions as Si atoms in a Si unit cell. The XRD peaks and the Cu_3Si planes in Figure 4-5 are indexed as the η' phase (rhombohedra, S.G. $R\bar{3}$, $a = 4.72 \text{ \AA}$, $\alpha = 95.72^\circ$).

Compared with the powder counterpart (JCPDS No. 51-0916), the η' (111) peak is significantly enhanced in all the samples examined, suggesting a preferred growth along the [111] direction. For Cu_3Si NTs grown on Si (111), η' (111) plane may establish epitaxy with Si (111) as illustrated in Figure 4-5(b). For Cu_3Si NSs grown on Si (100), on the

other hand the enhanced η' (111) diffraction implies a polycrystalline nature in accordance with the previous observation of pyramidal pits with $\{111\}$ Cu_3Si side surfaces formed on Si (100).^[246] Overall, the shapes of Cu_3Si nanostructures are well defined by the orientations of the Si substrates, although the Cu_3Si nanostructures may not be single crystals. As we will show later, an oxide layer was observed at the $\text{Cu}_3\text{Si}/\text{Si}$ interface, which excludes a complete epitaxial growth. Control experiments show that the top surfaces of nanostructures roughen further as the growth continues, indicating the formation of polycrystalline precipitates. Nevertheless, both the XRD data and the shape-controlled growth imply a partially crystalline nature of the Cu_3Si nanostructures, which is consistent with the previous reports on Cu_3Si precipitates in Si.^[245]

Spatially correlated SEM imaging and EDS mapping confirmed the Cu_3Si phase in the nanostructures as detected by XRD. To achieve better image quality, large-size

Figure 4-6 SEM images of Cu_3Si nanostructures and EDS element mapping of Cu and Si for (a) NT on Si (111), (b) NS on Si (100), and (c) NW on Si (110).

structures obtained by extending the growth time from 1 to 15 min (Figure 4-6) were chosen. The self-assembled structures are Cu rich; but the exact mole ratio between Cu and Si cannot be unambiguously determined due to the contribution of Si signal from the substrates.

Cross-section TEM imaging and EDS analysis were used to study the $\text{Cu}_3\text{Si}/\text{Si}$ interface and the growth mechanism. Several Cu_3Si NT samples were grown for 1 min with 15 nm Au NPs and were thinned for TEM observation. For the EDS analysis, Mo TEM grids were used in order to eliminate the Cu signal from the commonly used Cu grids. The cross-section image in Figure 4-7(a) suggests that an Au NP is buried inside the Cu_3Si NT. Because of its polycrystalline nature, Cu_3Si is more fragile than the single crystalline Si and Au. Since the sample preparation process involves dimpling and ion-mill thinning, special cares were taken to avoid sample amorphization. HRTEM image in Figure 4-7 (b) shows lattice fringes of Cu_3Si , and the SAED pattern indicates a crystalline nature. The structure is further confirmed by EDS mappings shown in Figure 4-7(c–f). Figure 4-7(d, f) suggests that the Au NP is also rich in Cu, which reflects their important role in absorbing and supplying Cu for the silicide reaction. The formation of the oxide layer in Figure 4-7(c), as defined by the higher oxygen intensity, is quite intriguing. Although there is always a native SiO_2 layer on Si wafer, it may not be the only source contributing to this oxide region. Si atoms in Cu_3Si are more active than those in pure Si in a wide range of temperature, and they are readily oxidized when exposed to air.^[247] Therefore, the oxide layer might be quite thin in the as-grown samples synthesized in an oxygen-poor environment. However, it is possibly thickened during the TEM sample preparation process comprising polishing, thinning, and air exposure. Near the

Figure 4-7 Cross-section TEM and EDS data of a Cu_3Si NT on Si (111) substrate.

(a) TEM image. (b) HRTEM image and SAED pattern corresponding to panel a. (c–f) EDS mappings of elements O, Cu, Si, and Au.

$\text{Cu}_3\text{Si}/\text{Si}$ interface, the oxidation product should be SiO_2 instead of CuO or CuO_2 because the bonding energy of $\text{Si}-\text{O}$ is larger than that of $\text{Cu}-\text{O}$. This is consistent with the XRD result that no CuO or CuO_2 peaks were found in Cu_3Si samples.

§ 4.3.2 Self-aligned Mg_2SiO_4 Nanowires

Unlike the Cu-related system, instead of nanoparticle structured products, self-aligned NWs are obtained on Si substrates with all surface directions when Mg vapor is supplied in the experiments. Extensive investigations revealed reproducible growth of NWs, which appear attached to the substrates. As shown in Figure 4-8(a–c), typically the NWs are several micrometers long and tens to a few hundred nanometers wide. The SEM images also suggest a clear correlation between the Si substrate orientations and the NW growth directions. By measuring the angles between the NWs and the primary flats of the

Figure 4-8 (a–c) SEM images of NWs grown on Si (110), (100), and (111) substrates, respectively. All scale bars represent 10 μm . (d–f) Corresponding schematics illustrating the NW growth directions. (g) Typical AFM image of NWs grown on Si (100) substrate. The height profile along the dashed line is shown in (h).

Si wafers, the NW growth directions are determined to be along Si $\langle 110 \rangle$. In particular, as illustrated in the schematic in Figure 4-8(d–f), the NWs are along Si $[1\bar{1}0]$ on Si (110), along Si $[01\bar{1}]$ and $[011]$ on Si (100), and along Si $[01\bar{1}]$, $[1\bar{1}0]$, and $[\bar{1}01]$ on Si (111). Occasionally, NWs deviating from the Si $\langle 110 \rangle$ directions were also observed. A typical AFM image of NWs on Si (100) is shown in Figure 4-8(g). The height profile in Figure 4-8(h) indicates that the NW width (100~200 nm) is about twice their height (60~80 nm). At high densities, NWs frequently come across their orthogonal neighbors, which sometimes terminate the NW growth. Similar phenomena also occur on Si (111) and (110) substrates.

XRD patterns of the as-grown samples on different Si substrates are shown in Figure 4-9(a). All the peaks related to the NWs can be assigned to Mg_2SiO_4 (forsterite, orthorhombic, $a = 0.598 \text{ nm}$, $b = 1.019 \text{ nm}$, $c = 0.476 \text{ nm}$, JCPDS No. 34-0189) and no magnesium oxide or silicide-related phase was observed. Forsterite is one of the main constituents of the earth's upper mantle and also exists in certain stellar sources. It has a high melting point of 1885°C and is a good insulator even at high temperature and under intense irradiation. Possessing low dielectric permittivity, high acoustic velocity, and good chemical stability,^[244] Mg_2SiO_4 is considered a promising candidate as a substrate and buffer layer in electronic and microwave devices, and as an active medium in tunable lasers.^[248] So far, there have only been a few studies on Mg_2SiO_4 nanomaterials, such as NWs, leaf-, and fishbone-like nanostructures.^[249-251]

Figure 4-9 (a) XRD pattern of Mg_2SiO_4 NWs grown on Si (110), (100), and (111) substrates. Powder diffraction data of forsterite (JCPDS No. 34-0189) is also shown. XRD peaks as a result of Si substrates have been subtracted for clarity. (b) Schematic illustrations of Mg_2SiO_4 epitaxially grown on Si (100). The sizes of the atoms are not drawn to scale.

Figure 4-10 (a) Cross-section SEM image of Mg₂SiO₄ NWs grown on Si (100). (b) Cross-section TEM image of one NW. (c–e) Corresponding EDS mappings of elements Mg, O, and Si. (f) Enlarged TEM image and SAED pattern. The zone axis is Si $\bar{1}10$. HRTEM images from the dashed box areas are shown in (g) and (i), highlighting the NW/Si interface and the twin boundary, respectively. (h) FFT image corresponding to panel (g).

In order to study the Mg₂SiO₄/Si interface, we thinned one sample grown on Si (100) using conventional TEM sample preparation techniques. Figure 4-10(a) shows a low resolution cross-section SEM image. Many Mg₂SiO₄ NWs were observed on the substrate surface, and the distance between two neighboring NWs varies from zero (merged together) to a few micrometer. The cross-section TEM image of one particular NW in

Figure 4-10(b) shows a sharp interface between the Mg_2SiO_4 NW and the Si substrate. The corresponding EDS mappings of Mg, O, and Si are shown in Figure 4-10(c–e). The magnified TEM image and the corresponding SAED pattern are shown in Figure 4-10(f), where the strong diffraction of the Si substrate overshadows the signal Mg_2SiO_4 . Nevertheless, the HRTEM image in Figure 4-10(g) taken at the interface region suggests that both the substrate and the NW are single crystalline with a thin amorphous layer of ~ 1 nm in between. The corresponding fast Fourier transform (FFT) image in Figure 4-10(h) indicates the following epitaxial relations: Mg_2SiO_4 [010] // Si $[\bar{1}01]$ and Mg_2SiO_4 (002) // Si (113) (see the illustration in Figure 4-9(b)). The lattice mismatch between $2 \times d[\text{Mg}_2\text{SiO}_4$ (002)] and $3 \times d[\text{Si}$ (113)] is $\sim 5\%$, which is quite large and probably the origin of the thin amorphous layer. A twin boundary was observed at the center of this NW, as shown in Figure 4-10(i). FFT analysis indicates that the epitaxial relationship of the left side is Mg_2SiO_4 (002) // Si $(\bar{1}\bar{1}3)$, which is equivalent to Mg_2SiO_4 (002) // Si (113) at the right side. This particular twinned Mg_2SiO_4 NW is a good example to illustrate the existence of two types of epitaxial relationship between Mg_2SiO_4 and Si.

§ 4.4 Discussions on Growth Mechanisms

§ 4.4.1 Endotaxial VLS Growth

Unlike the conventional VS and VLS growth mechanisms in the fabrication of various nanomaterials such as ZnO and SnO₂ NWs,^[112, 118-119] the growth of Cu₃Si and Mg₂SiO₄ nanostructures follows a more unusual route: endotaxial VLS mechanism.

Endotaxy indicates a specific kind of epitaxial growth, where the products are synthesized “in” the substrates instead of “on” them. To be accurate, substrates actively take part in the reaction and act as part of the source in the fabrication of the product structures. As illustrated in Figure 4-11, the as-grown structures consume part of the substrate material and lie on the rest part, looking as if they grow into the substrate.

In the growth of Cu₃Si nanostructures, Si wafers act as substrates and the source of Si atoms. The cross-section TEM images (Figure 4-7(a, b)) clearly indicate that the Cu₃Si NP is epitaxially grown in the substrate with part of its body buried below the wafer

Figure 4-11 Schematics illustrating the geometry of epitaxy and endotaxy, respectively.

surface, i.e., endotaxy growth.

In the case of Mg_2SiO_4 NW growth, however, the situation is a bit more complicated. Although the synthesis of Mg_2SiO_4 consumes Si in the substrate (since this is the only source of Si atoms), the $\text{Mg}_2\text{SiO}_4/\text{Si}$ interface rises higher under the NWs than the surrounding areas, as shown in Figure 4-10(b–e). Furthermore, the Si substrate surface becomes much rougher after growth, even at the regions without NWs, which indicates significant substrate etching. The substrate etching during the NW growth is related to the reaction between the Mg vapor and the Si substrate, which also explains the absence of any silicide formed in the Mg-related experiments. It is well known that Mg is very active on Si substrate and a reaction occurs at temperatures as low as 100 °C.^[252] However, because of the high vapor pressure of Mg (131 Pa at 600 °C, 2×10^4 Pa at 900 °C),^[253] in order to grow silicide by annealing Mg-coated Si substrates, capping layers are usually applied to prevent Mg evaporation.^[252] Even after the silicide formation, material loss may still occur since the eutectic temperature of the Mg–Si alloy is only 637.6 °C,^[244] which is much lower than the substrate temperature in our experiments. It has been suggested that the Mg–Si reaction could be effectively blocked by a thin layer of MgO.^[254] In our experiments, we found that if a high growth pressure is used, a thin MgO layer grows on the substrate surface and suppresses the substrate etching. We also carried out control experiments by partially covering Si substrates with a layer of 10 nm of MgO. The MgO film effectively protected the substrate from being etched, and the growth of Mg_2SiO_4 NWs was also suppressed.

This Mg-vapor-induced etching can also explain the M-shape interface profile under the NW in Figure 4-10(b). This M-shape suggests that this NW is a combination of two

single parallel ones. Since the NW diameter increases with time (will be shown later), the two NWs might be separated in the beginning, leaving the substrate in between subject to the Mg vapor etching, and consequently the valley-like Si profile was formed. As the growth progresses, they combined into a twinned NW because of the diameter increase. Our hypothesis is supported by the fact that the twin boundary sits exactly on the bottom of the valley, as shown in Figure 4-10(f).

Endotaxial growth has been observed before, especially in the silicide/Si systems. Self-aligned silicide nanostructures have also been fabricated,^[221-224] usually by the method of depositing metal on Si wafers and then annealing. In those experiments, Si wafers have to be thoroughly cleaned and have the native oxide layer removed. The reactions also need to be performed in ultra-high vacuum (UHV) chamber to suppress oxygen residues since oxide layer can efficiently block the diffusion of most metal elements into the wafers. In contrary, our experiments require much simpler equipment setup, thanks to the advantages of VLS growth route. Au NPs play key roles in the fabrication of both Cu_3Si and Mg_2SiO_4 nanostructures, not only as catalyst in VLS growth, but also in various other aspects.

§ 4.4.2 The Magic of Au NPs

Au NPs as VLS Catalysts

Au NPs play one common role in the growths of both Cu_3Si and Mg_2SiO_4 nanostructures, i.e., as catalyst in the VLS growths. In the growth of Cu_3Si nanostructures, Au NPs absorb Cu vapor and form Au–Cu alloy, enhancing the reaction between Cu and

Si around Au NPs. Our assertion is supported by the fact that Au NPs were detected inside the as-grown Cu_3Si nanostructures by both SEM (Figure 4-4) and TEM (Figure 4-7) observations. EDS mapping also indicates high ratio of Cu atoms inside the Au NPs after growth.

In the growth Mg_2SiO_4 NWs, Au NPs also act as the catalyst for VLS, absorbing Mg vapor and catalyzing its reaction with Si substrates. However, unlike Cu_3Si , Au NPs stay at the tips of Mg_2SiO_4 NWs and disappear after long time of heating. Details will be discussed later.

To verify the importance of Au NPs in these experiments, we carried out control experiments without Au NPs on Si substrate while keeping all other parameters unturned. As expected, no nanostructure was obtained on the substrates in both cases. When Cu vapor was supplied, the substrates remained intact after the growth. When Mg vapor was

Figure 4-12 Control experiments using 4 nm Au film as catalyst instead of Au NPs. (a, b) SEM images of the as-grown structures after heating in Cu and Mg vapor environments, respectively. Inset: XRD data corresponding to (b).

supplied, the substrate surfaces became rougher due to etching of Mg on Si, but no NW structure was observed.

On the other hand, although Au can be used as VLS catalyst in the growth of various nanomaterials, they are not necessarily in the form of NP at the beginning. For example, Au films have been used as catalyst to achieve the VLS growth of ZnO NWs (§3.2). Control experiments were also carried out using 4 nm Au film as catalyst in the growth of Cu- and Mg-related silicide nanostructures. As shown in Figure 4-12, instead of well aligned in-plane nanostructures, out-of-plane NPs and NWs were obtained in these control experiments. The compositions of the products are also proved to be different. For example, XRD result in the inset in Figure 4-12(b) indicates that MgO NWs were fabricated instead of Mg_2SiO_4 . Au thin film melts and forms nanodroplets at temperatures ($<500\text{ }^\circ\text{C}$ for 4 nm Au film, see Figure 3-6(a)) lower than the substrate temperatures in the experiments. Because the density of Au NPs formed this way is much higher than that of dispersed NPs, the spatial constraint on lateral growth and the insufficient supply of Si from the substrates presumably favor the growth of out-of-plane structures and suppress the in-plane growth of Cu_3Si NPs and Mg_2SiO_4 NWs.

Unique Roles of Au NPs in Cu_3Si and Mg_2SiO_4 Fabrications

Beside the application as VLS catalyst in the growth of Cu_3Si and Mg_2SiO_4 nanostructures, Au NPs also play some unique roles in each system, which prove to be critical to the morphologies and structures of the product nanomaterials.

In the synthesis of Cu_3Si nanostructure, besides absorbing Cu vapor, Au NPs play another crucial role in penetrating the oxide barrier, which makes the Cu/Si reaction

possible. It is known that Cu_3Si is the thermo-equilibrium phase and forms at the Cu–Si even at low temperatures. However, even a SiO_2 layer of only a few nanometers can block the diffusion of both Si and Cu, thus preventing the formation of silicides.^[255] In all previous reports using Si substrates as growth templates, the native oxide layer on Si must be carefully removed and the experiments were carried out in a UHV environment to minimize oxidation. In contrast, in our experiments, the Au NPs facilitated the Cu_3Si formation even in the presence of a SiO_2 barrier. A eutectic temperature of mere 363 °C allows Au and Si to form alloys.^[244] At high temperatures (>450 °C), Au NPs likely react with Si, and this reaction may force oxygen to diffuse deeper into the substrate or to release into vacuum, which effectively destroys the oxide layer.^[256-257] We conducted control experiments to evaluate the ability of Au NPs to penetrate through the oxide layer on the Si substrate. The diffusion of Au and Si and the reduction of SiO_2 are hindered if the oxide layer is too thick.^[257] Si (111) substrates with different oxide thicknesses (5, 10, 20, 50, and 100 nm) were prepared and used for the silicide growth. The formation of Cu_3Si NTs was terminated when the SiO_2 layer is thicker than 50 nm, which suggests that the diffusion through the SiO_2 layer is a limiting factor in the silicide growth.

The growth route of Mg_2SiO_4 NWs is distinctive from that of Cu_3Si . Careful SEM observations were carried out at different growth stages by controlling the synthesis time. Figure 4-13 presents the schematic of the proposed growth process and the corresponding SEM images of the sequence. Step 1: Au NPs are dispersed on Si substrates. Under the high temperature environment in the furnace tube, the molten Au NPs continuously absorb Mg vapor and simultaneously catalyze the NW synthesis. Step 2: Directional in-plane growth of the NW catalyzed by the Au NPs which stay at the growth front during

Figure 4-13 (a) Schematics illustrating a three-step mechanism proposed for the in-plane growth of Mg_2SiO_4 NW. The NW growth under the presence of Mg vapor is catalyzed by the Au NPs, and it is terminated when the Au NPs are exhausted. (b–d) Typical SEM images corresponding to the steps 1–3 in (a). Inset in (c) shows a NW with an Au NP sitting at its tip. The scale bar in the inset is 100 nm.

the growth. Step 3: Au NPs gradually shrink during growth and their exhaustion eventually terminates the NW growth. Since the vapor pressure of Au is very low (5.44×10^{-5} Pa at 1200 K),^[253] the Au NPs are not likely to evaporate in our experiments. The shrinkage of the Au NPs may be related to fast diffusion of Au on Si surfaces, i.e., Au atoms continuously leave the NPs during the NW growth process, which has been previously reported by Hannon *et al.* and Kawashima *et al.*^[155, 258] The NW diameter reduction during growth helps us to determine the growth direction of the NWs, e.g., from left to right in Figure 4-13(a).

Different from the fabrication of Cu_3Si nanostructures, the ability of Au NPs to

penetrate the native oxide layer on Si substrates is not as important in the growth of Mg_2SiO_4 NWs. Native oxide layer cannot impede the reaction between Mg vapor and Si substrate, evidenced by the remarkable substrate etching during the experiments. However, Mg_2SiO_4 component is only formed on the migration path of the Au NPs, indicating other distinctive roles of Au NPs in the NW growth other than merely absorbing Mg vapors.

We can understand of the Mg–Si–O reactions from several aspects by considering their ternary phase diagram shown in Figure 4-14.^[259] In contrary to many other refractory metal–silicon–oxygen systems, e.g., Mo–Si–O and Ta–Si–O,^[260] Mg can readily form stable phases with Si and O, such as Mg_2SiO_4 and MgSiO_3 . There is no stable tie line between Mg and SiO_2 , which indicates chemical reactions between the two phases will occur when sufficient thermal energy is supplied to the system, i.e., at sufficiently high temperature. It is consistent with our experiment that the native SiO_2 on

Figure 4-14 Calculated Mg–Si–O phase equilibria at 25 °C.

the substrates does not block the reaction between Mg and Si. Although the MgO–Si and MgO–SiO₂ systems appear to be stable at room temperature from the phase diagram, Kamitsuji *et al.* found that reactions actually take place at high temperatures (>800 °C) to form Mg₂SiO₄.^[261]

The reactions responsible for the Mg₂SiO₄ formation may have several possible multi-step paths. Both MgO and Mg₂Si may serve as the intermediate reactants; however, their absence in the final products, indicated by the XRD and TEM results, suggests that Mg₂SiO₄ is the most stable phase under the experimental conditions used in our experiments. We should also point out that the MgSiO₃ phase was also detected in control experiments when the partial pressure of oxygen is sufficiently low; such a reduction environment can be created, for example, by adding H₂ in the carrying gas (data not shown). This is not surprising since Mg₂SiO₄ and MgSiO₃ are positioned quite close to each other in the phase diagram (Figure 4-14). Even the residual oxygen in the carrying gas of pure argon is sufficient to sustain the formation of Mg₂SiO₄. On the other hand, if 0.5% O₂ was deliberately added to the carrying gas, the Mg₃N₂ source would be oxidized quickly, which suppressed any NW growth.

In summary, in both Cu- and Mg-related systems, Au NPs play a similar role of initiating the growth under the presence of corresponding metal vapor. However, they possess distinct features related to the growth mechanism and the product morphologies. First, in the Cu₃Si experiments, NSs, NTs, and NWs were grown on Si (100), (111), and (110) substrates, respectively, and their edges are along Si <110>. In the Mg₂SiO₄ experiments, only NWs were observed and their growth is along Si <110> directions. Second, in the growth of Cu₃Si nanostructures, Au NPs do not move and are buried inside

the Cu_3Si nanostructures. In contrast, Au NPs stay at the top of the Mg_2SiO_4 NWs, and the VLS NW growth effectively propels the Au NPs to move along Si $\langle 110 \rangle$. Finally, in contrast to the growth of Cu_3Si nanostructures where the Au NPs are preserved in the nanostructures, Au NPs diffuse away during the growth of Mg_2SiO_4 NWs, which eventually terminates the NW growth.

§ 4.4.3 Growth Control of the Nanostructures

While the shape and morphology of the as-grown Cu_3Si and Mg_2SiO_4 nanostructures are determined by the orientations of the Si substrates, we have also systematically tuned the growth parameters to control their dimensions and achieve better understanding of the

Figure 4-15 Size control of the Cu_3Si nanostructures by adjusting Au NP diameter and growth time at 960 °C.

growth mechanism.

Cu₃Si Experiments

The effects of mainly two parameters were studied, namely, the Au NP size and the heating time. Au NPs with diameter of 4.8 ± 1.2 , 13.5 ± 1.0 , and 37.0 ± 2.0 nm were used and the heating duration at 960 °C was varied from 0 to 3 min. The growth started before the temperature reached 960 °C and Cu₃Si nanostructures were observed in all the experiments. Statistical results on the dimensions of these nanostructures are summarized in Figure 4-15. Generally speaking, the nanostructure sizes increase with larger Au NP diameter or longer growth time, which offers additional controls on the synthesis. With

Figure 4-16 SEM images of Cu₃Si structures fabricated with different growth time. 5 nm Au NPs were used as catalysts and the growth temperature was kept at 960 °C.

larger Au NPs, the length of the NWs reaches tens of micrometers, while the width remains around 500 nm.

When the growth time exceeds 30 min, flowerlike fractal patterns appear on triangle and square surfaces, and the nanowire surfaces become very rough, as shown in Figure 4-16. The formation of such branched fractal patterns indicates a nonequilibrium growth with oscillatory nucleation.^[262] The small size of Au NPs and their localized absorption of Cu vapor may also cause nonuniform growth of polycrystalline products; this tendency become more pronounced when the Cu_3Si structures grow larger. Furthermore, the phase change during cooling may cause nonuniform distribution of strains and contribute to the structural distortion and the formation of polycrystalline structures. When the size of the triangle exceeds 3 μm , the surface roughening is quite significant; its boundary, however, remains well defined. This robust shape control might be a result of the strong orientation dependence of the diffusion of Si atoms, in line with our proposed growth mechanism.

Mg_2SiO_4 Experiments

Similar systematical studies were also performed in the Mg_2SiO_4 experiments. The default growth parameters are the following: Au NP size = 25 nm, source-substrate distance = 2 cm, source temperature = 915 °C, pressure = 10 mbar, and growth time = 30 min. These parameters were adjusted individually to isolate their effects on the NW growth.

As expected, increasing the density of the catalyst consistently leads to more NWs, as shown in Figure 4-17. The effects of growth temperature and time were also studied. We selected Si (110) to achieve statistics considering that the NWs run parallel on (110)

with little mutual interaction between the NWs. It would be much more challenging to quantitatively study the NWs grown on Si (111) and (100) since the NWs sometimes switch their growth directions or merge with each other. Nevertheless, the effects of various parameters present similar trends for all three types of substrates. The temperature window for effective NW growth is quite narrow, i.e., 900~950 °C. The effects of three source temperatures of 905, 915, and 925 °C were compared and are shown in Figure 4-18(a). The lengths of the NWs were measured after different growth times (the growth time refers to the duration for which the system was kept after reaching the set temperature). The evolution of the NW length can be roughly divided into three regimes. In the first 5 min, the growth rate is larger at higher temperatures, which is due to the fact that at the early stage a higher temperature generates a higher Mg vapor pressure and larger Au mobility, thus increasing the NW growth rate. In the second growth regime, the rate significantly decreases at the higher temperatures and after ~15 min the NW length for 905 °C catches up with that for 925 °C. This behavior can be attributed to the faster exhaustion of the Au NPs at higher temperatures. In the final stage, after ~20 min the NW length gradually saturates for all three temperatures and the complete exhaustion of the Au NPs terminates the NW growth. As delineated in Figure 4-18(b), the growth temperature and time have less an effect on the width of the Mg_2SiO_4 NWs. The NWs grow wider at higher temperatures, possibly because more Mg vapor induces larger liquid-state alloy droplets. The NW width also noticeably increases with time, because the NWs are more likely to merge when they are longer, which also contributes to larger statistical uncertainty.

Figure 4-18(c–f) show the dependence of the NW dimensions on the growth pressure,

Figure 4-17 Effect of Au NP density on the growth of Mg_2SiO_4 NWs. (a–c) Mg_2SiO_4 NWs catalyzed by low-density Au NPs on Si (110), (100), and (111) substrates, respectively. (d–f) Results obtained by using higher (approximately by 10 times) Au NP densities. All the scale bars represent the same length.

the Au NP size, and the substrate position, i.e., the distance between source and substrate. Among these factors, the substrate position has the most prominent effect on the NW dimensions. Since the substrates were placed closely within a narrow range of 2.5 cm, the variation of the substrate temperature is less than 10 °C by calibration and may not play the dominant role. Instead, the key factor could be the Mg vapor pressure, which has a notable dependence on the location. At positions further away from the source, weaker Mg vapor induces shorter and thinner Mg_2SiO_4 NWs, which may be attributed to the smaller Au–Mg alloy droplets. We varied the growth pressure from 5 to 15 mbar and

Figure 4-18 Systematic studies on controlling the growth of Mg_2SiO_4 NWs. (a–b) Effects of growth temperature and time on the NW dimensions. (c–f) Effects of growth pressure, substrate position, and Au NP size on the NW dimensions.

selected Au NPs with diameters from 5 to 90 nm. Although higher ambient pressures and larger Au NPs usually induce longer NWs, their effects are relatively weaker. Similarly, we did not find any strong dependence of the NW width on the growth pressure and Au NP size.

§ 4.5 Conclusion

In this chapter, we introduced the fabrication of self-aligned Cu_3Si and Mg_2SiO_4 nanostructures by vapor transport method. When Cu vapor is supplied, Cu_3Si NTs, NSs, and NWs are grown on Si (111), (100), and (110) substrates, respectively. The sides of the NTs and NSs and the length of the NWs are all aligned to Si $\langle 110 \rangle$ directions. When Mg vapor is supplied, in-plane Mg_2SiO_4 NWs are obtained on Si substrates of all directions. All the NWs follow the Si $\langle 110 \rangle$ specific directions. The shapes and morphologies of the nanostructures are controlled by substrate orientation. On the other hand, we have also achieved precise control on their sizes and dimensions by systematically tuning various experiment parameters including Au NP size, growth temperature and growth time.

Au NPs play key roles in the synthesis of these nanomaterials. Firstly, Au NPs act as the catalyst in the VLS grow mechanism. At high temperature, Au NPs absorb Cu or Mg vapors and initiate the growth of corresponding nanostructures. In the growth of Cu_3Si , Au NPs also help to break the barrier of native oxide layer on Si wafers, which could effectively block the reaction between Cu vapor and Si atoms below. In the growth of Mg_2SiO_4 , Au NPs melt and diffuse along the substrate surface. The synthesis of Mg_2SiO_4 compound also requires the existence of Au as catalyst, otherwise Si substrate would be etched without any product left. Thus the growth of Mg_2SiO_4 NWs is a result of Au catalyzed synthesis and the surface diffusion of Au that happens simultaneously.

Our achievements on controlled fabrication of silicide nanomaterials extend their applications. For example, by coating the as-grown Mg_2SiO_4 NW samples with 10 nm Au film and then immersing in HF (5M) + H_2O_2 (0.5M) solution at room temperature for 30 min, well-structured Si nanowalls can be fabricated, as shown in Figure 4-19. It is well

Figure 4-19 (a, b) 20 °tilted SEM images of vertical Si nanowalls fabricated on Si (100) and (110) substrates, respectively. (c, d) Corresponding cross-sectional SEM images. Insets: schematics illustrating the morphologies of the Si nanowalls.

known that noble metals (e.g., Au, Ag, and Pt) can catalyze directional etching in Si in HF solution.^[263-265] In our experiments, Mg_2SiO_4 NWs work as the “mask” to protect Si below from the Au-catalyzed HF etching, thus producing Si nanowalls.

Our work is also important as fundamental research on the growth mechanisms in nano-fabrications. The increased knowledge about endotaxial VLS mechanism, which involves the reaction between catalyst, source vapor, and substrate, may help the understanding and designing novel functional nanomaterials and devices.

Chapter 5

Conclusion

In this dissertation, we studied the fabrication of various semiconductor nanomaterials and silicide related nanostructures via vapor transport method. Our interests are focused on the fundamental growth mechanisms and the controlled synthesis of these nanomaterials by tuning catalyst, doping, and adjusting various other growth parameters.

Vapor-liquid-solid (VLS) and vapor-solid (VS) are two dominant growth mechanisms in nanofabrication via vapor transport routes. By VLS mechanism, the growths of the nanostructures (mostly nanowires, or NWs) are controlled by the sizes and positions of the catalyst nanodroplets. On the other hand, VS growth may induce more complicated nanostructures, such as heterostructures like nanocombs. Selective control on the growth mechanism in nanofabrication is still an open question.

We started by discussing this topic through growth of ZnO NWs. ZnO nanostructures have been extensively studied for several decades as an important semiconductor material. ZnO NWs are easy to fabricate by various methods. Most information on the structure and property of ZnO are very clear and it is one of the best candidates to study the nanofabrication mechanisms. We purposely compare the performances of three catalysts (Au, Ag, and Pt) at two growth temperatures (ZnO mix graphite source powder, 800 °C; pure Zn source powder, 500 °C) in the growth of ZnO NWs. Although the existence of the catalysts is essential to the NW growth in all cases, VLS only occur in the high temperature growth using Au or Pt as catalyst. We found that

the failure of catalyst liquification (such as Ag being oxidized at high temperatures) and the high Zn vapor pressure (when using pure Zn powder as source material) may suppress VLS and induce VS dominant ZnO NW growth.

Element doping is an important technique in material science. It can be used to tune the physical and chemical properties of specific materials without significantly affecting their atomic structures. For example, the carrier type and concentration in Si wafer can be tuned by various doping elements such as phosphor. In our studies, we found that element doping may also have strong effect on the morphologies and growth mechanisms of the nanomaterial fabrications. In this thesis we show two typical examples of Cu doped ZnO and Ti doped SnO₂ nanostructures.

Cu doping in ZnO nanostructures were realized by adding CuCl₂ into the source powders (previously pure Zn). By this method, Cu doped ZnO nanoneedles and nanonails were fabricated instead of nanowire structures (using pure Zn source). Their morphologies (nanoneedle and nanonail) can be controlled by the position of the substrate, which is related to the partial pressure of oxygen. At a specific substrate position, continues morphology evolution from nanoneedle to nanonail can be observed on one single substrate (less than 1 cm in length).

Ti doped SnO₂ nanostructures were realized by adding TiO₂ into the source powders (SnO₂ mix graphite). Adding TiO₂ into the source reliably change the product morphology from nanowires to nanobelts. The growth mechanism was also changed from self-catalyzed VLS (pure SnO₂ nanowire growth) to VS (Ti doped SnO₂ nanobelt growth). Similar to the Cu doped ZnO nanostructures, we believe that doping modifies the surface energies of their crystal structures, thus inducing the morphology changes in the product

nanostructures. Beside the doping effects, we are also able to control the lateral size of the SnO_2 nanowires and nanobelts over two orders of magnitude by tuning other experiment parameters. As a result, we have achieved the thinnest SnO_2 nanowires and widest SnO_2 nanobelts reported so far.

Finally, silicide related nanomaterials grown on Si substrates caught our interests. Silicide materials are important in the applications of semiconductor industries. On the other hands, bottom-up growths of silicide related nanomaterials are strongly related to the Si substrates, which act as both substrates and source of the Si atoms. Substrate induced morphology control (such as self-assembled features) of silicide nanomaterials have been reported before. However, the lack of further controls on the size and position of the as-grown structures limit their application. In our experiments, we used vapor transport approach to grow silicide related nanomaterials. Au nanoparticles (NPs) were used as catalyst and played key roles.

We selected the growth of Cu_3Si and Mg_2SiO_4 nanostructures as two typical examples. Cu vapor was generated by heating mixed CuO/graphite source powder. At high temperatures ($>800^\circ\text{C}$), Cu vapor reacts with Si substrates and forms Cu_3Si nanostructures with the help of Au NP catalysts. The as-grown nanostructures show substrate orientation dependence, long range ordering, and self-assembled features. That is, Cu_3Si nanotriangles, nanosquares, and nanowires were grown on Si (111), (100), and (110) substrates, respectively. The boundaries of these nanostructures are all along Si $\langle 110 \rangle$ specific directions. Au NPs melt and absorb Cu vapor during the growth, like their role in the conventional VLS mechanism. On the other hand, Au NPs were also critical to break the barrier of native oxide layer on Si substrates, which may effectively block the

Cu/Si reactions. Thus it is possible to control the position of the Cu_3Si nanostructures by controlling the positions of the pre-deposited Au NPs.

Mg_2SiO_4 NWs were fabricated by supplying Mg vapor, which was generated by the decomposition of Mg_3N_2 source powders at high temperatures ($>600^\circ\text{C}$). Interestingly, the as-grown NWs were self-assembled along one, two, and three directions on Si (110), (100), and (111) substrates, respectively. Careful studies indicate that they all follow Si $\langle 110 \rangle$ specific directions. Au NPs absorbed Mg vapors, and catalyzed their reactions with silicon and oxygen to form Mg_2SiO_4 . On the other hand, melting Au NPs show high mobilities on Si surfaces. The surface diffusion of Au NPs induced the nanowire structure of the products.

The synthesis of Cu_3Si and Mg_2SiO_4 nanostructures follow an unconventional in-plane VLS growth mechanism. The catalyst NPs may move (in the growth of Mg_2SiO_4 NWs) or not move (in the growth of Cu_3Si NPs) during the growth. The application of VLS approach is extended from the conventional out-of-plane nanowire growth.

In summary, we have studied the fabrication of several semiconductor and silicide related nanomaterials via a simple vapor transport route. We discussed their growth mechanisms and the feasibility of precise control on structure, morphology, and size of the product nanomaterials. We will continue to work on other nanomaterials to study fundamental physics in nanostructures and try to solve the open question of precise controlled fabrication of predesigned nanomaterials and functional nanodevices. Exploration of the functionalities of these nanomaterials in a wide range of applications is out of the scope of this thesis, but it warrants further efforts.

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