Synthesis, Electrical and Optical Characterization of Semiconductor Nanowires

Dissertation

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Abstract

Over the past 15 years, nanowires (NWs) and nanotubes have drawn great attention since the application of VLS growth mechanism into the synthesis of one dimensional structures. Semiconductor nanowires exhibit novel electrical and optical properties. With a broad selection of composition and band structures, these one-dimensional semiconductor nanostructures are considered to be the critical components in a wide range of potential nanoscale device applications. To fully exploit these one-dimensional nanostructures, current research has focused on synthetic control of one-dimensional nanoscale building blocks, characterization of their novel properties, device fabrication based on nanowire building blocks, and integration of nanowire elements into complex functional architectures. Progress has been made in past two decades. However, there are still challenges in NWs growth controls, such as size, shape, position, stoichiometry and defects. Due to the dimensionality and possible quantum confinement effects of nanowires, there are also challenges in characterization and device fabrication.

A systematic study of controlled growth of nanowires has been conducted in this dissertation. The first part of this dissertation presents various synthesis techniques of semiconductor nanowires via metal catalyzed vapor-liquid-solid (VLS) growth mechanism. Pulse laser deposition (PLD) with arsenic over pressure method has been successfully utilized for GaAs nanowires. Challenges such as uniformity issue commonly
seen in MOCVD and MBE systems, morphology and stoichiometry issues commonly seen in conventional PLD systems have been overcome. Si nanowires fabrication via ultrahigh vacuum magnetron sputtering has reported for the first time, which also provides an alternate route for Si nanowires synthesis.

The second part of this dissertation discusses optical properties of ensemble direct band gap nanowires. Photoluminescence spectra have been measured on an ensemble of random orientated InP nanowires. Polarization anisotropy has been explored on ensemble nanowires and oxide-coated nanowires. Our calculation for randomly oriented nanowires agrees well with experimental results. The control of polarization anisotropy of nanowires is realized by coating nanowires with an oxide layer composed of matching dielectric constant media. This opens a path to optical spin injection and detection on direct band gap nanowires.
Dedication

Dedicated to my parents and fiancée
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Field of Study

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Chapter 1

Introduction

Nanotechnology has been an exciting and rapidly expanding area of research for more than a decade [1-3]. The fundamental interests come from the fact that nanometer is the length scale that bridges the microscopic world where the behavior of matter needs to be treated in quantum mechanics and the macroscopic world where quantum mechanics reduces to classical physics. Studies on the preparation, structure, and properties of nanostructures have been carried out with collective efforts that cross borders between many areas of physical sciences, engineering and biological sciences [4].

Nanostructures can be defined as systems in which the physical size in at least one- dimension (1D) is less than 100nm. As shown in Fig. 1.1, reducing 1, 2 and 3 dimensions of bulk materials to the nanometer scale produce nanometer thick two-dimensional (2D) structures such as graphene and quantum wells (QWs) [5, 6], one-dimensional (1D) carbon nanotubes (CNTs) [7], nanowires [4], zero-dimensional (0D) Fullerenes [8] and Quantum Dots (QDs) [9], respectively. Dimensionality plays a critical role in determining the properties of nanostructures. True low-dimensional materials should have infinitesimal sizes in one or more dimensions as suggested by their ideal geometry. In reality, nanostructures always have finite size and it is impossible to completely isolate a system from interaction with environment, therefore, the prefix
“quasi” is often added to describe the low-dimensional structures prepared in the real world. Studies on low-dimensional nanostructures have revealed fascinating properties. For examples, studies of 2D electron gas in semiconductor hetero-structures have led to remarkably rich and often unexpected results such as the quantum-Hall effect [10].

Fig. 3.1 Nanostructures (a) 2-D graphene and quantum wells; (b) 1-D carbon nanotubes and nanowires; (c) fullerene and 0-D quantum dots

The properties of nanostructures are not only dependent upon dimensionality but also determined by their physical size. When the size of a structure larger than a certain characteristic length scale, the properties approach the corresponding bulk values; on the other hand, when the size of the structure is smaller or comparable to the characteristic
length scale of some property, then that property is confined and size dependent. The characteristic length scales depend on materials and specific properties. Many fundamental properties of bulk materials are characterized by length scales on the order of 1 to 100 nm. As an example of size-dependent properties of nanostructures, the photoluminescence emission of semiconductor 2D quantum wells [11], nanowires [12], and 0D nanocrystals [13] exhibit systematic blue-shift when their physical sizes are smaller than 5-20 nm, the exciton diameters of corresponding bulk semiconductor materials.

Interest in nanostructures has been driven by not only fundamental sciences but also their potential applications. First, nanostructures are very promising materials for future electronics. Utilizing a “bottom-up” approach [14, 15] to create and assemble devices from a specific arrangement of atoms or molecules has the potential to overcome the limitations of the conventional “top-down” lithographic approaches by providing a methodology for control over lattice compositions, scaling of devices to the molecular scale, and minimal surface roughness. In particular, semiconductor nanowires and carbon nanotubes [4] offer a unique approach for the bottom-up assembly of electronic and photonic devices with the potential for on-chip integration of non-silicon based photonics with silicon nano-electronics. The unique geometries of NWs and CNTs enable them to function as both active device elements and interconnects, which can lead to highly integrated device structures. For example, semiconductor nanowires have been used for assembling a range of functional devices, including FETs, p-n diodes, inverters and logic circuits [16].
Secondly, low-dimensional nanostructures can be used to fabricate functional photonic devices. For examples, light-emitting diodes (LEDs) and laser diodes made of semiconductor quantum wells have long been commercialized. Ensembles of semiconductor nanocrystals, which exhibit well-understood size-dependent optical properties, have been used to fabricate LEDs. Stimulated emission at wavelengths tunable by the nanocrystal diameter has also been achieved. Moreover, nanoscale photodetectors made of individual nanowires and crossed nanowire $p$-$n$ junction LEDs have been demonstrated [17].

1D semiconductor nanowires are the smallest dimension structures that can be used for efficient transport of carriers and optical excitations. An important advantage of 1D nanowires over other low-dimension materials is that nanowires can function as both active device elements and interconnects carrying current to and from devices. Although previous results have highlighted the promised of assembly of nanowires into electronics and optoelectronic devices, developing a fundamental understanding of the electrical and optical properties of nanowires remains absolutely essentials for defining future applications.
Chapter 2

Fabrication Techniques

2.1 Introduction to 1D nanostructure growth

2.1.1 Symmetry breaking

In general, the growth of 1D material requires that two dimensions are kept in the nanometer scale while the third dimension extends to macroscopic dimensions. This overall requirement is considerably more difficult than corresponding constrains needed for 0D and 2D structures [18]. To achieve 1D growth in systems where atomic bonding is relatively isotropic requires that the growth symmetry must be broken rather than simply isotropic growth at an early stage.

Numerous efforts have been placed on the bulk synthesis of NWs, and various strategies have been developed to break the symmetry either physically or chemically [4]. A common theme is the use of linear template, including the edges of surface steps [19], nano fibers [20], and porous membranes [21] to direct chemical reactions and materials growth in 1D. This strategy is conceptually simple but also limited in that resulting NWs are usually polycrystalline, which could limit their potential for many applications. Also, there are difficulties associated with removing from the template for various applications.
Fig. 2.1 Schematic illustration of six different strategies that have been demonstrated for achieving 1D growth: a) dictation by the anisotropic crystallographic structure of a solid; b) confined by a liquid droplet as in the vapor-liquid-solid process; c) direction through the use of a template; d) kinetic control provided by a capping reagent; e) self-assembly of 0D nanostructures; and f) size reduction of a 1D microstructure [4].

Over past years, another general strategy has been developed which involving exploiting a catalyst to confine growth in 1D. Depending on phase involved in the reaction, this approach in typically defined as vapor-liquid-solid (VLS) [14], solution-liquid-solid (SLS) [22] or vapor-solid (VS) growth [23].
2.1.2 Vapor-liquid-solid growth with catalyst

Among all vapor-based methods, the VLS method is currently the most successful approach for generating single-crystal semiconductor nanowires in large quantities. In VLS mechanism [14], a catalyst serves as a nanocluster or nanodroplet that defines the diameter of a growing NW and serves as the site that preferentially directs the addition of reactants to the end.

This synthetic concept is especially important since it readily provides the intellectual underpinning needed for the specification of the catalyst and growth conditions required for predictable NW growth. First, equilibrium phase diagrams are used to determine catalyst materials that form a liquid alloy with the NW materials of interest. The phase diagram is then used to choose a specific composition and growth temperature such that there is a coexistence of a liquid alloy and a solid phase. Therefore, this temperature is normally limited to the range between the eutectic temperature and melting point of NW materials. The liquid catalyst alloy cluster serves as preferential site for absorption of reactants since the sticking coefficient is much higher on liquid surface than on solid surface. Once the liquid catalyst alloy cluster is supersaturated, the nucleation site starts crystallization. Preferential 1D growth occurs in the presence of reactants as long as the catalyst nanodroplet remains in the liquid state. Within this framework, it is straightforward to synthesize NWs with different diameters and compositions, if appropriate nanoscale catalyst clusters are available.
VLS growth mechanism was developed and applied in whisker growth by Wagner although the whisker size is usually at micrometer scale. The minimum radius of whiskers is defined by equilibrium thermodynamics:

$$r_{min} = \frac{2\sigma_{LV}V_L}{RT\ln\sigma}$$

(2.1)

where $\sigma_{LV}$ is the liquid-vapor surface free energy, $V_L$ is the molar volume of liquid, $\sigma$ is the degree of supersaturation, $R$ is the gas constant and $T$ is the temperature. For most materials, the minimum critical radius is about 100nm for $\sigma=1.02$. Increasing supersaturation in liquid can reduce the stable liquid droplet size only to very limited extent since it can also result in homogeneous condensation of NW materials into unwanted particles. In the past decade, constraint of equilibrium thermodynamics has been overcome in a general way by either employing laser ablation to produce nanometer-size particles, using self-assembled particles from thin metal film annealing [24], or chemically synthesized nanoparticles as catalytic clusters [25].

All major steps involved in a VLS process are illustrated in Fig.2.2, for the growth of GaAs nanowire [26]. Based on GaAs-Au phase diagram as shown in Fig.2.2, GaAs and Au form liquid alloys when the temperature is above eutectic point (630 °C). Once the liquid droplet is supersaturated with GaAs, nanowire growth will start to occur at the solid-liquid interface. The establishment of the symmetry-breaking solid-liquid interface is the key step for the one-dimensional nanocrystal growth in this process.
2.2 Fabrication Techniques

In order to study experimentally electrical and optical properties in semiconductor nanowires, the first step is the synthesis of nanowires. Many fabrication techniques have been successfully developed. Some common methods include molecular beam epitaxy (MBE) [27], sputtering, thermal evaporation [28], chemical vapor deposition (CVD) [29],
Metalorganic chemical vapor deposition (MOCVD) [30], and pulse laser deposition [15]. Additional structures can be accomplished by optical lithography, electron-beam lithography, thermal treatments, and chemical methods. Each technique has its advantages and disadvantages. High-quality samples require proper fabrication techniques and a thorough understanding of the fabrication processes.

In this chapter, we will discuss some of the fabrication techniques used in our research, including sputtering, pulse laser deposition (PLD), molecular beam epitaxy (MBE), chemical vapor deposition (CVD), Metalorganic chemical vapor deposition (MOCVD) and optical lithography.

### 2.2.1 Sputtering

When the surface of a material is bombarded by high energy positive ions, it is possible to cause the ejection of the surface atoms. This process is commonly known as (cathode) sputtering. The ejected atoms can condense on a substrate to form a film or nanowires with the help of catalysts.

The mechanism of sputtering is often called knock-on sputtering. The elementary event is an atomic collision cascade. The incident ions bombard the atoms in the target, causing the ejection of the atoms. The history of sputtering dates back to 1877 when sputtering was used to coat mirrors. Sputtering has many advantages compared to other thin films fabrication techniques, including high deposition rate, the ability to produce insulating and metallic materials, uniformity of thickness, good adhesion to most surfaces,
and maintaining the stoichiometry of the target composition [31]. As a result, sputtering has become one of the most versatile techniques in thin film fabrication in both industry and research labs. Meanwhile, sputtering provides an alternative way for nanowire synthesis.

### 2.2.1.1 Sputtering fundamentals

The sputtering process consists of the following stages, (1) ionization of sputtering gas, usually an inert gas, such as argon; (2) acceleration of ions towards the target; (3) collision between the ions and the atoms in the target; (4) the ejection of atoms from the target; (5) deposition of sputtered atoms onto the substrate.

The electrons in the plasma acquire energy from the applied electric field and collide with the gas molecules. When the energy of the electrons $E_e$ is lower than 2 eV, the collisions are elastic. At $E_e$ higher than 15 eV, the collisions result in ionization, which sustains the plasma by producing positive ions and new free electrons, as described by the following equation

$$ A + e^- \rightarrow A^+ + 2e^-, \quad (2.2) $$

where $A$ is the gas molecule. When $E_e$ is between 2 eV and 15 eV, a variety of inelastic collisions take place, which result first in the excitation in the gas molecule. The relaxation of an electronically excited state is practically instantaneous ($\sim 10^{-8}$) in most cases and is accompanied by the emission of a UV or visible photon, which gives the plasma its glow.
The condition of self-sustained plasma depends on the geometry of the sputtering chamber, gas pressure, and the voltage between the electrodes. The mean free path, the mean distance that a particle traverses in a gas between collisions with the gas molecules, is an important parameter. Normally the gas pressure is less than $10^{-1}$ torr, in which gas can be treated as ideal gas. Hence, the mean free path of molecule in molecule-molecule collision $l_m$ can be expressed as [32]

$$l_m = \frac{RT}{\sqrt{2\pi a^2 P N_A}}$$  \hspace{1cm} (2.3)

where $a$ is the diameter of the gas molecule. Different types of sputtering require different gas pressure, which can be as low as $5 \times 10^{-5}$ torr for magnetron sputtering and as high as 100 mtorr for a simple DC diode sputtering system.

### 2.2.1.2 Types of sputtering

Over the years, several types of sputtering have been employed for the deposition of thin films by sputtering. The simplest is “diode” direct current (DC) sputtering, in which the material to be deposited (target) is connected to a negative voltage and the substrate is mounted on the anode facing the target. A DC voltage of the order of 1 - 5 kV is applied across the cathode (target) and the anode with current density 1 – 10 mA/cm$^2$. The plasma is sustained with a gas pressure of 10 - 100 mTorr. At pressures below 10 mTorr, the plasma cannot be self-sustained because of insufficient ionizing collisions. If the gas pressure is too high, the ions are slowed by inelastic scattering and will not have enough energy to produce secondary electrons when they hit the target.
During the deposition of the films using diode sputtering, substantial number of inert gas molecules is known to be trapped in the films. In addition, the deposition rate for DC sputtering is very low.

An alternative method to increase the ionization at low pressure is to supply additional electrons from a source other than the target. This is called the triode sputtering. The extra electron source is a hot cathode, usually a heated tungsten filament, which can withstand ion bombardment for a long time. The density of ions in the plasma is controlled by adjusting the electron emission current of the hot filament. This method allows sputtering at a pressure of the order of 1 mTorr, much lower than that in the diode sputtering. The limitation of this technique is the complexity of power supplies and the difficulty in producing uniform sputtering from large flat targets [31].

The most important and widely used sputtering technique today is magnetron sputtering, which has made significant progress since its development in early 1970s. It has a number of advantages over the conventional sputtering techniques, particularly with respect to high deposition rate, low operating pressures, and much better overall quality of the films.
Fig. 2.3 is the schematic diagram of the electrodes in a typical magnetron sputtering system. The target is clamped to a planar cathode backed by permanent magnets and soft magnetic materials (e.g. Fe) that produce a toroidal magnetic field with field lines above and approximately parallel to the cathode surface. Usually, the permanent magnets are typically Nd-Fe-B magnets, which can produce a magnetic field of a few hundred Gauss near the cathode surface. In order to have higher sputtering
efficiency, the top layer of the cathode shown in Fig.2.3 is made as thin as possible, e.g.
0.125 mm, to achieve high magnetic field on the cathode surface. Some sputter source
manufacturers offer exposed magnets in order to maximize the magnetic field above the
target. The voltage applied to the target produces an electric field approximately
perpendicular to the magnetic field near the cathode surface. The secondary electrons in
the region where electric (E) and magnetic (B) fields are nearly perpendicular are trapped
into toroidal orbits, thus, greatly increase the ionization efficiency, as shown in Fig. 2.4.

![Diagram](image)

**Fig. 2.4**: Schematic diagram of the top of the gun. The electric field E and the magnetic
field B are approximately perpendicular to each other. Electrons travel in helical paths.

Most magnetron sputtering systems operate in the pressure ranging from 1 to 20
mTorr and a cathode voltage of a few hundred volts. The sputtering rates are primarily
determined by the ion current density at the target. The deposition rates of the films are
affected by the ion current density, target-substrate distance, gas pressure, target material, and sputtering gas composition.

The plasma is confined above the target by the magnetic field, but small amounts of ions can still bombard other parts of the sputtering gun. To alleviate this problem, the gun cover and the shield are electrically grounded. To prevent the side of the gun from bombardment by ions, the ground shield (also the top cover) is very close to the gun, with spacing around 1 - 3 mm. Therefore no ions will be present between the gun and the grounded shield and the gun is protected from the sputtering process.

Finally, a combination of triode and magnetron sputtering can further increase the ionization efficiency. With an additional cathode electron source added to magnetron sputtering system, extra electrons increase the plasma density. The deposition rates can be up to 10 times higher than that of the conventional magnetron sputtering at the same voltage. The operating pressure can also be greatly reduced to as low as 0.05 mTorr at full power. At such a low pressure, the mean free path of Ar molecules, $l_m$, is 1 m. The atoms from the target can reach the substrate without scattering from the gas molecules.

2.2.1.3 Si nanowire synthesis via sputtering system

We have synthesized Si nanowires using ultrahigh vacuum (UHV) sputtering. Si nanowires with diameters of 200–300 nm were obtained on thermally oxidized Si substrate using Au(15Å)/Si(8Å)/Au(15Å) trilayer as catalysts. Si nanowires with diameter between 50 and 100 nm and length up to 8 µm were synthesized using epitaxial
growth on Si (111) substrates. Sputter provides an alternative fabrication route for Si nanowire synthesis to more commonly used CVD and PLD techniques. More details will be discussed in Chapter 5.

2.2.2 Pulsed laser deposition

2.2.2.1 Fundamentals of pulsed laser deposition (PLD)

PLD has been used to deposit high-quality films and nanostructures for more than a decade [33]. The technique uses high power (typically 1–5 J/cm²) laser pulses to melt, evaporate and ionize material from the surface of a target. The threshold power density needed to produce such a plume depends on the target material, its morphology, and the laser pulse wavelength and duration, but might be of the order of $5 - 10 \times 10^7$ W/cm² for ablation using ultraviolet (UV) excimer laser pulses of 10 ns duration. This ablation event produces a transient, highly luminous plasma plume that expands rapidly away from the target surface. The ablated material is collected on an appropriately placed substrate upon which it condenses and the film grows.
2.2.2.2 General procedures of PLD

The process of PLD can generally be divided into four steps: (1) laser ablation of the target material and creation of plasma; (2) dynamic of the plasma; (3) deposition of the ablation material on the substrate; (4) nucleation and growth of the film on the substrate surface. [34]

2.2.2.2.1 Laser ablation of the target and creation of a plasma

The ablation of the target material upon laser irradiation and the creation of plasma are very complex processes. The removal of atoms from the bulk material is done by vaporization of the bulk at the surface region in a state of non-equilibrium and is
caused by a coulomb explosion. In this stage the incident laser pulse penetrates into the surface of the material within the penetration depth. This dimension is dependent on the laser wavelength and the index of refraction of the target material at the applied laser wavelength and is typically in the region of 10 nm for most materials. The strong electrical field generated by the laser light is sufficiently strong to remove the electrons from the bulk material of the penetrated volume. This process occurs within 10 ps of an ns laser pulse and is caused by non-linear processes such as multi-photon ionization which are enhanced by microscopic cracks at the surface, voids, and nodules, which increase the electric field. The free electrons oscillate within the electromagnetic field of the laser light and can collide with the atoms of the bulk material thus transferring some of their energy to the lattice of the target material within the surface region. The surface of the target is then heated up and the material is vaporized. This laser energy could be equivalent to dozens of eV per atom. The remaining energy should be enough to surpass the melting and ionizing points, resulting in excited plasma over a very small volume. This inevitably leads to an expulsion of target atoms away from the surface in a highly forward directed plasma plume.

In order to prevent the target from being asymmetrically deprived of material, which could result in a change in plume direction, the target can be rotated slowly. This partially corrects the problem, and also improves target utilization.

Another common effect, which was a fact for every deposition in this work, is that when the target is ablated by the beam, the chemical composition is altered. This sometimes results in a more metallic composition on the very surface of the target. If this
metal happens to reflect ultraviolet light, the amount of energy absorbed will be progressively less with each turn.

2.2.2.2 Dynamic of the plasma

The material expands in the form of plasma parallel to the normal vector of the target surface towards the substrate due to Coulomb repulsion and recoil from the target surface. The spatial distribution of the plume is dependent on the background pressure inside the PLD chamber. The density of the plume can be described by a $\cos(\theta)^n$ with a shape similar to a Gaussian curve, where $n$ can vary from approximately 4 to 30, and $\theta$ is measured with respect to the normal of the surface [35].

2.2.2.3 Macroscopic factors of nucleation on substrate

The nucleation process and growth kinetics of the film depend on several growth parameters including:

1. Laser parameters – several factors such as the laser fluence [Joule/cm$^2$], laser energy, and ionization degree of the ablated material will affect the film quality, the stoichiometry, and the deposition flux. Generally, the nucleation density increases when the deposition flux is increased.
(2) Substrate surface temperature – The surface temperature has a large affect on the nucleation density. Generally, the nucleation density decreases as the temperature is increased.

(3) Substrate surface – The nucleation and growth can be affected by the surface preparation (such as chemical etching), the miscut of the substrate, as well as the roughness of the substrate.

(4) Background pressure – Common in oxide deposition, an oxygen background is needed to ensure stiochiometrically transfer from the target to the film. If, for example, the oxygen partial pressure is too low, the film will grow off stiochiometry which will affect the nucleation density and film quality.

### 2.2.2.2.4 Nucleation and Growth Modes

Atoms adhere to the surface due to attractive forces with electrochemically compatible and/or similar atoms. The exact nature of the bonding depends once again on the type of material. Since atoms adhere to the surface, this process is called adsorption, and the accumulated atoms themselves may be called adatoms. These adatoms interact with the top substrate atoms, and with each other.

The substrate in most cases needs to have a higher temperature than room temperature. Otherwise, the surface may be too cold, and adatoms may not have enough kinetic energy to arrange freely to a stable equilibrium. This may result in the film being completely amorphous or highly defective, even though the stoichiometry should suggest
a more stable configuration. Once the adatoms are on the surface of a heated substrate, several things may occur. They may, and probably will nucleate with each other. The opposite may occur, called dissociation, which happens due to thermal vibration.

Adatoms may diffuse around the surface until they find a stable configuration. The adatoms may even evaporate from the substrate itself. There are several models that describe the possible growth mechanisms when substrates are being continuously bombarded with new atoms. These models can be divided as various general types [32]:

(1) Simple growth mode – It can assume that every atomic site in the substrate is equivalent, and may hold one adatom. The atoms are absorbed into an immobile state, which in turn can absorb another atom. Since there is no interaction between sites, this should result in a distribution of randomly piled up stacks of adatoms, as can be seen in Fig. 2.6. This is the model that roughly resembles a substrate that is too cold during the deposition.
Fig. 2.6 (Top) Simple growth model – Randomly stacked piles of adatoms over the substrate surface (Bottom) Visual interpretation and comparison of three growth models in thin films: Frank-van der Merwe growth model, Volmer-Weber growth model and Stranski-Krastanov growth model [32]

(2) Frank-van der Merwe growth model – In this model the dominant factor is the total surface energy of the configuration, meaning that each site is not independent of their neighbor. Therefore, the most electrochemically stable stacking of adatoms is the one with least surface area. Adatoms will then arrange each other over one single monolayer at a time. In order for this to begin, the adatom-surface interaction must have a much stronger than adatom-adatom interactions
(3) Volmer-Weber growth model – If the adatom-adatom interactions are much stronger than the interactions with the substrate surface, this must lead to the formation of 3-dimensional adatom clusters. In comparison to the Frank-van der Merwe model, many layers should stack up in order to unite all the separate islands over the substrate. Only high temperature and surface energy equilibrium may be able to produce a flat surface on the resulting film.

(4) Stranski-Krastanov growth model – If the adatoms, like in the Frank-van Merwe model, have a much stronger attraction towards the surface than toward each other, then the first few atomic layers of the film will also be stacked up one single layer at a time. This model on the other hand predicts that once the atoms are stacked up to a certain point above the substrate, maybe even a single monolayer, the adatoms start to pile up and eventually start growing as separate three-dimensional islands similar to the Volmer-Weber model.

2.2.2.3 Nanowire growth via PLD

Since 1998 when Charles Lieber’s group firstly synthesized Si nanowires with pulsed laser deposition via VLS mechanism [15], nanowires and hetero-structures of nanowires of many semiconductor materials have been synthesized with this method. In Chapter 4, we have systematically studied the synthesis conditions for GaAs nanowires using PLD with various arsenic over-pressures. Arsenic over-pressure with As$_2$ molecules is introduced into the system by thermal decomposition of polycrystalline GaAs. Long single-crystal GaAs nanowires with uniform diameter, small diameter
distribution and thin surface oxide layer were obtained. Our approach to InP nanowires will be discussed in chapter 6.

2.2.3 Chemical vapor deposition

2.2.3.1 Fundamentals of CVD

CVD is a thin film deposition technique in which volatile precursors are reacted on a substrate and grow a thin film of the desired material. In a typical CVD process, a substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. Frequently, volatile byproducts are also produced, which are removed by gas flow through the reaction chamber. CVD has proven to be useful in the fabrication of solid state electronic devices as it can provide excellent coverage of substrate features and can deposit high quality thin films of various materials over a large area. The ability to easily control doping levels in thin film growth is advantageous for studying the solubility levels of impurity atoms in materials.
Fig. 2.7 Activation-energy diagram for a chemical reaction [32].

In order for the chemical reaction and deposition of films to occur, the reactants (gas molecules in the gas-phase reactions) must gain at lease a certain energy $E_{a+}$, which is called activation energy in the forward direction (reactants $\rightarrow$ products), either from heating or from collisions. Fig. 2.7 shows the activation-energy diagram for a CVD process. The reverse reaction direction (products $\rightarrow$ reactants) requires a higher activation energy $E_{a-}$ than $E_{a+}$. Thus, the reaction is energetically favorable in the forward direction, where $\Delta_r H_0$ is the heat of reaction.

A number of processes can happen simultaneously at the surface of the substrate, including the adsorption of source gases, surface diffusion of the gas molecules, reaction of the adsorbates with each other and with the surface, and desorption of gaseous by-product. As the gaseous reactants arrive at the surface of the substrate, a fraction of them are physically adsorbed by the surface and the others are immediately reflected from the surface. Some adsorbates may subsequently desorb from the surface without reaction.
The rest of the adsorbates react with each other or with the surface and are chemically bonded to the surface. Some of the products may undergo reverse reactions and desorb.

Table 2.1 lists some common overall chemical reactions used in CVD. Those overall reactions usually consist of a series of reaction steps, some in the gas phase and some on the surface of the substrate. For example, the deposition of Si from Silane involves many reactions, as shown in Fig. 2.8.

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal decomposition</td>
<td>CH$_4$(g) $\rightarrow$ C (diamond or graphite) + 2H$_2$(g)</td>
</tr>
<tr>
<td></td>
<td>2CrO$_3$(g) $\rightarrow$ 2CrO$_2$(c) + O$_2$(g)</td>
</tr>
<tr>
<td>Oxidation</td>
<td>SiH$_4$(g) + 2O$_2$(g) $\rightarrow$ SiO$_2$(c) + 2H$_2$O(g)</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>2AlCl$_3$(g) + 3H$_2$O(g) $\rightarrow$ Al$_2$O$_3$(c) + 6HCl(g)</td>
</tr>
<tr>
<td>Reduction</td>
<td>WF$_6$(g) + 3H$_2$(g) $\rightarrow$ W(c) + 6HF(g)</td>
</tr>
<tr>
<td>Displacement</td>
<td>Ga(CH$_3$)$_3$(g) + AsH$_3$(g) $\rightarrow$ GaAs(c) + 3CH$_4$(g)</td>
</tr>
</tbody>
</table>

Table 2.1 Typical overall chemical reactions used in CVD
2.2.3.2 Procedures of CVD

In CVD, the gases containing the elements to be deposited enter a chamber, within which the substrate of a specific material is maintained at a suitable temperature. The gases react to form a solid film on the substrate surface. The chemical reactions taking place is very important in all CVD processes. Flow rate, gas composition, substrate temperature, gas pressure, and chamber geometry are all crucial variables for the deposition, the composition, and the quality of the film.
The basic CVD process includes eight steps as listed in Fig. 2.9. (1) Mass transport of the reactant gases from the gas inlet to the reaction zone, where the reaction zone is a narrow region close to the surface of the heated substrates; (2) Gas phase reactions in the reaction zone that lead to the formation of film precursors; (3) Mass transport the film precursors to the growth surface; (4) Adsorption of the film precursors onto the growth surface; (5) Surface diffusion of the precursors to the growth sites; (6) Reaction of precursors at the surface and film growth on the substrates; (7) Desorption of
the by-products of surface reactions; (8) Mass transport of by-products from the reaction zone to the main gas flow that exhausts from the reactor [36].

The source gases usually begin to decompose or react with each other in the gas phase when heated to certain temperature at some point during their transport to the substrate and before they adsorb on the surface of the substrate. Generally, the products of these reactions are more reactive with the substrate than the source gases. For example, in the deposition of Si from silane as shown in Fig. 2.8, SiH$_4$ can absorb on the substrate surface and then decompose to form Si film. Or SiH$_4$ reacts in a few steps to produce SiH$_3$ which absorbs and decomposes to form Si film on the substrate. The reaction rate from SiH$_3$ is higher than that from SiH$_4$.

2.2.3.3 Advantages and disadvantages of CVD

CVD has advantages over other fabrication techniques. These include (1) uniform coating over large area, including non-planar substrates, (2) premixing of gases to avoid compositional gradient of alloys across the substrate, (3) source replenishment that is less frequent and does not require breaking vacuum, (4) selective-area deposition only on activated surface area, (5) high deposition rates, (6) etching of deposited film by introducing partial pressure of a suitable chemical etchant, (7) simple vacuum system due to high operating pressure [32].

There are also certain disadvantages about CVD. The most serious concern is safety because most of the gases used in CVDs are poisonous or flammable, and some of
them are extremely toxic. Thus, great cares need to be taken for the operation of CVD systems.

2.2.3.4 Nanowires synthesis via CVD system

CVD system is widely used in synthesis of Group IV nanowires such as Si[29] and Ge[37]. The gold nanocluster catalysts with diameters ranging from 2 – 50 nm were dispersed on oxidized silicon substrates followed by UV-ozone cleaning of the substrates. Then, the substrates were placed in a quartz reactor at the downstream end of the furnace, and the furnace was evacuated to less than several mTorr. The reactor was heated to 435 °C under H₂, followed by 30 min with a 6-sccm flow of SiH₄ (50% in He) and a 60-sccm flow of H₂ with the growth pressure maintained at 100 Torr, resulting in the synthesis of Si NWs [29].

2.2.4 Metal Organic Chemical Vapor Deposition (MOCVD)

2.2.4.1 Fundamentals of MOCVD

Metal organic chemical vapor deposition (MOCVD), also known as metal organic vapor phase epitaxy (MOVPE), is a chemical vapor deposition method in which the surface reaction of metal organics and metal hydrides, both in vapor phase, take place on a heated substrate.

Since its invention in 1968, MOCVD has become a dominant epitaxial growth technique in the compound semiconductor industry [38]. Epitaxy refers to a special case
of thin film deposition in which both the deposited thin film and the substrate are single crystalline materials. Compared to another technique, molecular beam epitaxy (MBE), MOCVD has the advantage of higher throughput, lower maintenance cost and ease of incorporation for phosphorous containing compound. Today, it is the dominant epitaxial technology for photonic devices such as laser diode, light emitting diode (LED) as well as electronic device such as heterojunction bipolar transistor (HBT). Beside III-V semiconductors, MOCVD has also proved versatile for II-VI, and IV-IV compound semiconductors [39].

2.2.4.2 MOCVD System Setup

Most MOCVD systems consist of three parts, gas handling system, reactor, vacuum and exhaust system, as shown in Fig. 2.10.

![Fig. 2.10 Schematic of a MOCVD system setup](image)
(1) Gas handling system: Gas is introduced via devices known as 'bubblers'. In a bubbler a carrier gas (usually nitrogen or hydrogen) is bubbled through the metalorganic liquid, which picks up some metalorganic vapor and transports it to the reactor. The amount of metalorganic vapor transported depends on the rate of carrier gas flow and the bubbler temperature, and is usually controlled automatically and most accurately by using a Piezocon type vapor control system. The mixing of volatile alkyl and hydride compounds in the gas handling system is achieved within a manifold that first stabilizes the flows, then mixes them and selectively directs them either to the reaction chamber or into the vent (waste). The manifold is designed to uniformly mix metalorganic and hydride sources prior to reaching the growth zone.

(2) Reactor: The reactor chamber is usually made of quartz or stainless steel and contains the susceptor on which the substrate wafer is resting. The susceptor can be heated using one of the following three methods: RF induction heating, radiative (lamp) heating, or resistance heating. The shape of the reactor chamber is carefully designed and engineered to eliminate the development of vortices and dead volumes. The growth parameters (e.g., pressure, temperature, and total gas flow) are chosen such that a laminar flow free of convection is realized. This is generally easier to do by operating at low pressure. By doing so, one ensures that a stable, reproducible, and uniform growth process is achieved.

(3) Vacuum and exhaust system: MOCVD system for GaAs and InP use toxic materials like AsH₃ and PH₃. The exhaust gases still contain some non-reacted AsH₃ and PH₃, which need to be converted to liquid or solid wastes for recycling (preferably) or disposal.
2.2.4.3 Growth mechanism

In MOCVD system, crystal growth process is governed by law of thermodynamic and kinetic processes. Thermodynamics determines the driving force for the overall growth reaction while kinetics defines the rates at which various steps occur. In this growth process, one or more of the Group III constituents are transported to the reaction zone in the form of metal alkyls, while the Group V constituents are usually transported as hydrides. Binary compound is the simplest case which involves a reaction of the vapors of a volatile metal organic compound and a gaseous hydride, given by

\[ R_nM + XH_n \rightarrow XM + nRH \uparrow \]  \hspace{1cm} (2.4)

where R is an organic radical (tertiary-butyl-, methyl- or ethyl-radical), M and X are the constituent Group III and V species respectively for the deposited solid.

During the epitaxial growth, the group V concentration is always kept in excess compared to group III concentration due to its higher volatility. As a result, the growth rate is limited and controlled by the concentration of group III alkyl elements. Like most CVD process, the growth regimes of the MOCVD process can be defined in three regions as shown in Fig. 2.11 [40].

The alkyl pyrolysis efficiency profile is steep at the growth temperature below 500°C. This implies that the growth is reaction-rate limited at temperature < 500°C. For substrate temperature of 500°C and higher, the alkyl pyrolysis efficiency attains unity. The growth regime of this temperature range (500°C - 800 °C) is mass transport limited [41, 42]. For temperature above 800°C, the gas phase pyrolysis of hydrides become important and solid particulate can be formed before reaching the substrate. This is known as parasitic spontaneous nucleation or pre-reaction. Moreover, when temperature
approaches the congruent temperature of III-V alloys, the semiconductor begin to decompose into its constituent gas phase. This reduces the growth rate and an increased vapor pressure from the constituent source is needed to maintain smooth surface morphology.

Fig. 2.11 Growth rate as a function of temperature showing the three distinct growth of a typical III-V semiconductor synthesis in MOCVD systems [40].

Some of the III-V Semiconductors grown by the MOCVD process are listed in Table 2.2, which is shown below:
<table>
<thead>
<tr>
<th>Compound</th>
<th>Reactants</th>
<th>Growth Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>TMGa + AsH₃</td>
<td>650–700</td>
</tr>
<tr>
<td>GaP</td>
<td>TMGa + PH₃</td>
<td>750</td>
</tr>
<tr>
<td>GaN</td>
<td>TMGa + NH₃</td>
<td>1000–1050</td>
</tr>
<tr>
<td>GaSb</td>
<td>TEGa + TMSb</td>
<td>500–550</td>
</tr>
<tr>
<td>AlAs</td>
<td>TMAI + AsH₃</td>
<td>700</td>
</tr>
<tr>
<td>AlN</td>
<td>TMAI + NH₃</td>
<td>1100–1200</td>
</tr>
<tr>
<td>InAs</td>
<td>TEIn + AsH₃</td>
<td>650–700</td>
</tr>
<tr>
<td>InP</td>
<td>TEIn + PH₃</td>
<td>725</td>
</tr>
</tbody>
</table>

Table 2.2 Reactants and growth temperatures for some of the III-V semiconductors grown by the MOCVD Process

Under condition of excess group V hydrides and while in mass transport limited growth regime, the growth rate of binary alloy is given by [43]:

\[
R_g = \frac{M A P_A F_A}{k T d_A A_e}
\]  

(2.5)

where \(M_A\), \(P_A\), \(F_A\), \(k\), and \(T\) are molecular weight, vapor pressure, and flow rates of alkyl metal respectively; \(k\), \(T\), and \(A_e\) are Boltzmann's constant, bubbler temperature, and effective area of growth chamber respectively.

Generally, the rate of growth can be estimated by using a simple formula as [43]:

\[
R_g = \frac{P_A F_A}{22400 (B_A - P_A)}
\]  

(2.6)

where \(P_A\), \(F_A\), and \(B_A\) are alkyl vapor pressures (torr), alkyl-hydrogen flow rate (cm³/min), alkyl bubbler pressure (torr) respectively; the unit of growth rate is mol/min.
The Surface morphology of III-V compound semiconductor strongly depends on V/III ratio. As a rule of thumb, the higher V/III ratio, the smoother is the crystal morphology. However, increasing V/III ratio also reduces the surface mobility of group III gives rise to non-stoichiometric structure and causes point defects in the epitaxial layer [44]. In a typical system, PH$_3$/AsH$_3$ and V/III ratios are in the range of 25-50 and 40-100 respectively. As we discussed previously, the decomposed efficiencies of alkyl metals and hydrides strongly depend on the growth temperature profile, so the optimal PH$_3$/AsH$_3$ or V/III ratio is a function of the substrate temperature.

2.2.4.4 Advantage and disadvantage of MOCVD system

The MOCVD growth technique has proved advantageous in terms of multiple-hetero-structure growth control, high versatility, high uniformity of composition, material morphology, sharp interfaces, and the ability to control solid composition while maintaining good lattice matching. Even for lattice-mismatched material systems such as III-nitrides, this method has been proven to produce high-quality layers.

However, MOCVD still suffers from the highly toxic, flammable, pyrophoric, and corrosive nature of the reactants (such as arsine and phosphine) and byproducts. Like any other CVD process, the high temperatures needed to decompose a molecule in MOCVD sometimes lead to substantial diffusive rearrangement of both dopants and the semiconductor species in hetero-structures. This rearrangement produces a blurring of the intended composition profiles or even the out-diffusion of species from the back of the wafer into the vapor and back into the growing epilayer (autodoping). Furthermore, in
MOCVD, one controls what enters the reactor but not what arrives at the growing semiconductor surface. A change in the incoming gas chemistry does not produce a corresponding change at the surface. A delay and a time averaging will result [40].

2.2.4.5 Nanowire synthesis via MOCVD system

In 2003, P.D. Yang’s group firstly reported high quality GaN nanowires using a metal-initiated MOCVD approach [45]. Trimethylgallium (TMG) and ammonia source materials were used as Ga and N precursors. A 2-10 nm thin film of Ni, Fe, or Au was thermally evaporated onto a silicon substrate or c-plane and a-plane sapphire substrates. Subsequent vapor-liquid-solid growth of GaN nanowires occurred at a substrate temperature of 800-1000 °C. The reaction was carried out in an oxygen-free environment at atmospheric pressure. TMG was kept cool in a -10 °C temperature bath. Nitrogen, used as a carrier gas, was percolated through the TMG precursor and coupled with a second nitrogen line to give a total nitrogen flow rate of 250 sccm. These were supplied via quartz tube. Hydrogen and ammonia sources were supplied via a quartz tube at a total flow rate of 155 sccm. The deposition generally took 5-30 min. One unique feature of these MOCVD GaN nanowires is that they are well-facetted and most of them have triangular cross sections.
2.2.5 Molecular Beam Epitaxy (MBE)

2.2.5.1 Fundamentals of MBE

Molecular beam epitaxy (MBE) is an advanced technique for the growth of thin epitaxial layers and nanostructures of compound semiconductors, Si, Ge and other materials [46]. For MBE system, the growth is conducted under an ultra-high vacuum of $10^{-8} \sim 10^{-9}$ Pa. Under such a high vacuum, O$_2$, CO$_2$, H$_2$O, and N$_2$ contamination on the growing surface can be neglected. This makes it possible to reduce the growth rate down to nm/min, so that precise control of the growth thickness is possible. Another important advantage of MBE is that in-situ monitoring of the growing surface is possible. Reflection high-energy electron diffraction (RHEED) is one of the most powerful tools used to see the flatness and atomic structure of the surface during growth. MBE can produce high-quality single crystal layers with very abrupt interface, monolayer control of thickness, precise doping and compositional accuracy. Because of the high degree of control and flexibility using MBE, it is a valuable tool in the development of sophisticated, magnetic and photonic devices [47, 48].
2.2.5.2 MBE System Setup

The schematic of typical MBE system is shown in Fig. 2.12 [47, 49, 50]. An MBE system is basically made up of five parts: 1) an ultra-high vacuum chamber equipped with wafer transfer and rotation mechanism, 2) a heated sample mount, 3) source cells, 4) in-situ monitoring tools, which are used to monitor the initial surface cleaning and successive growth, and 5) pumps, which provide and keep the UHV necessary for growing high-quality materials.

Source cells can be effusion cells, which generate component fluxes by evaporating or subliming high purity source materials, or gas cells, which generate component hydride or plasma fluxes controlled by a mass flow controller. The hydrides decompose at the substrate surface and incorporate into grown materials without extra
hydrogen atoms. Growth from hydrides, the substrate surface will be covered by hydrogen and this makes surface reaction kinetics different from the cases without surface-H coverage. In hydride gas source growth, source hydrogen desorption is normally the rate limiting step, as it is believed in Si growth from disilane (Si₂H₆).

The in situ monitoring tool include reflection high-energy electron diffraction (RHEED), which provides information about substrate surface configuration and flatness; pyrometry, which provides in situ growth temperature calibration; and residual gas analyzer (RGA), which provides information about chamber vapor composition for chamber leakage detection and growth monitoring. More complex MBE systems may also contain Auger electron spectroscopy (AES), electron energy-loss spectrometry (EELS), and low energy electron diffraction (LEED), which provide composition and chemical status analysis, localized vibrational modes of adsorbed molecules as well as surface phonon analysis, and two dimensional surface configuration analysis, respectively.

The pumps include ion pumps, cyro-pumps, turbo pumps, and a liquid nitrogen cyro-shroud, which is maintained below nitrogen boiling point and surround the hot source furnaces and inner growth space to decrease chamber outgassing.

2.2.5.3 Growth mechanism of MBE

The major difference between MBE and other epitaxial growth techniques stems from the fact that the growth is carried in an ultrahigh vacuum environment. Therefore,
the growth is far from thermodynamic equilibrium conditions and is mainly governed by the kinetics of the surface processes. This is in contrast to the other growth techniques, such as LPE and VPE, in which the growth conditions are near the thermodynamic equilibrium and are controlled primarily by diffusion processes near the surface of the substrate. The most important processes in MBE growth occur at the atomic level in the crystallization zone and can be summarized into four fundamental steps, as illustrated in Fig. 2.13: (a) the adsorption of the constituent atoms or molecules impinging on the substrate surface; (b) the surface migration and dissociation of the absorbed species; (c) the incorporation of the constituent atoms into the crystal lattice of the substrate or the epilayer, at a site where sufficiently strong bonding exists; that site is usually at the edge of a spreading atomic layer, the growing epitaxial crystal; and (d) the thermal desorption of the species not incorporated into the crystal lattice [49].

Fig. 2.13 Schematic illustration of the surface processes during MBE epitaxial growth [49].
The atoms impinging on the substrate surface must be allowed sufficient time to reach their proper position at the step edge before an entire new layer comes down and buries them. Otherwise, we would get a very rough surface with mountain-like and valley-like features on it. Worse yet, the crystal could actually end up with defects, such as missing atoms at sites in the crystal structure that would result in undesirable electrical properties.

Within the ultrahigh vacuum, the atoms in the chamber have a long mean free path, and collisions with other atoms are infrequent before reaching the substrate. Atoms from the sources are thus able to travel in a straight line until they collide with the substrate material. The mean free path $L$ of an atom is related to the concentration $n$ of this species and its atomic or molecular diameter $d$ through the relation:

$$L = \frac{1}{\sqrt{2\pi n d^2}} \quad (2.7)$$

The concentration $n$ is determined by the pressure $P$ and temperature $T$ in the MBE:

$$n = \frac{P}{k_b T} \quad (2.8)$$

where $k_b$ is the Boltzmann constant. Under ultrahigh vacuum conditions ($10^{-10}$–$10^{-11}$ Torr), the mean free path of gases is found to be several orders of magnitude higher than the distance between source and substrate (~10–20 cm).

Due to its ultrahigh vacuum growth environment, one of the primary advantages of MBE systems is the ability to use advanced in situ characterization tools such as reflection high-energy electron diffraction (RHEED), auger electron spectroscopy (AES), X-ray photoelectron spectroscopy, low-energy electron diffraction, secondary-ion mass spectroscopy, and ellipsometry, in order to monitor the film growth process [47].
In a RHEED system, a beam of electrons with energies in the range of 5 to 50 keV is directed on the substrate at a grazing angle \( \theta \) as shown in Figure 2.14. The electrons are then diffracted by the epitaxial wafer surface, which leads to the appearance of intensity-modulated streaks on a fluorescent screen, is called a RHEED pattern. There are two types of RHEED characterization: static and dynamic. For static REED as shown in Fig. 2.14, the atomic construction of the surface can be determined from the RHEED diffraction pattern. Such information is of particular interest since the atomic surface construction is a function of the flux of the incoming electron beam, the substrate temperature, and the strain of the epilayer. Dynamic RHEED is based on the change of the intensity of the main (central) diffraction streak as the wafer surface roughness changes over time, which is shown in Fig. 2.15. Indeed, during the epitaxial growth process, starting from an atomically flat surface, the roughness of the epitaxial layer increases as a new atomic layer nucleates. Once the surface coverage reaches 50%, the roughness is maximal and will start to decrease as the growing layer is filled. Once the new layer is completed, the roughness is minimal and will start to increase again. The intensity of the main RHEED streak thus follows this periodic oscillating pattern during growth, with the maximal intensity corresponding to the minimal roughness. The time separation between two adjacent peaks yields the time required for the growth of a single layer of the crystal. This is a powerful method that provides an accurate thickness calibration technique that is sensitive to within one single atomic layer.
Fig. 2.14 Schematic diagram of the geometrical configuration of Static RHEED measurements [49].

Fig. 2.15 Illustration of the mechanism for Dynamic RHEED specular spot oscillations during growth of a monolayer; $\theta = 1$ means one full layer is covered on the substrate. [51]
2.2.5.4 Advantage and disadvantage of MBE system

In MBE system, the growth is conducted in ultra high vacuum of up to $10^{-9}$ - $10^{-11}$ Torr. Under such high vacuum, O$_2$, CO$_2$, H$_2$O, and N$_2$ contaminations on the growth surface can be negligible. This makes it possible to reduce growth rate down to nm/min, which allows films to grow epitaxially.

Thanks to its ultrahigh vacuum growth environment, one of the primary advantages of MBE systems is the ability to use advanced in-situ characterization tools such as reflection high-energy electron diffraction (RHEED) to monitor the film growth process. Intensity oscillation of RHEED signals accurately measure the growth rate $\AA/sec$.

There are two major disadvantages for MBE system: high costs associated with maintaining the ultrahigh vacuum environment and rather slow growth rate. In addition, technological challenges remain, such as alleviating the difficulty associated with growing phosphorous-bearing alloys such as InP and InGaAsP; and alloy composition control.

2.2.5.5 Nanowires synthesis via MBE system

Due to MBE ultra high vacuum working environment and well controlled growth rate, it is a great advanced technique for the growth of Si, Ge and other compound semiconductor nanowires. For example, Liu et al synthesized Si nanowire on Au/Si (111) substrate by gas source MBE in 1999 [52]. A 15 nm gold layer was deposited on Si (111) wafer which is prepared using a standard Shiraki Clean method. Then the substrate was
loaded into growth chamber with base pressure of $10^{-10}$ Torr, which is much lower than conventional CVD. The substrate temperature was raised to 900°C over a period of 2 hours and heated at this temperature for 20 min, without any source gases present, in order to form a Au/Si eutectic and to remove any surface oxide. The wire growth was performed by introducing pure Si$_2$H$_6$ at a pressure between $1 \times 10^{-4}$ and $1 \times 10^{-7}$ Torr, and at temperatures ranging from 600 to 800°C. Improved uniformity in length is found by using MBE when compared with CVD Si nanowire growth, which is mainly due to the relatively lower gas pressure.
Chapter 3

Characterization Methods

3.1 Introduction

Characterization of materials provides information about structural, electrical, chemical, optical, and other properties, which determine the quality of the samples and their applications. This chapter focuses on the relevant methods used by the author to characterize structural, morphological, compositional, optical, and transport properties of the samples made by the techniques mentioned in the previous chapter.

3.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) has unique capabilities for analyzing surfaces. SEM has a much better resolution than the optical microscope because the wavelength of electrons is only 0.2 Å at energy of 10 keV, while the wavelength of the visible light is a few thousand Å. The practical magnification and resolution limits of SEMs are ~ 300,000 X and 10 Å, compared at 2000 X and 2000 Å of an optical microscopes [53].
The basic SEM consists of four components:

(1) The imaging system produces an electron beam and focuses it onto sample.

(2) The detector system analyzes the signal released by the sample during electron bombardment.

(3) The display system shows the image of the sample.

(4) The vacuum system keeps the sample chamber in high vacuum (~ $10^{-6}$ Torr), otherwise, electrons will be scattered by the gas molecules.
3.2.1 Imaging system of SEM

Fig. 3.1 is the schematic of the SEM imaging system [54]. The electron gun and several lenses produce a collimated, coherent beam of electrons which can be focused onto the sample. The scan coils can move the electron beam across the sample in a square or rectangular pattern. The electron gun consists of three parts: a filament, which generates electrons, an aperture shield, and an anode held at a positive high voltage with respect to the filament, which can accelerate electrons to a few tens of keV. The conventional filament is made of tungsten, which is easy to operate and maintain. The non-conventional electron sources include LaB$_6$ and field-emission guns, which give better resolution but pose higher requirement in the vacuum and maintenance, resulting higher cost. Typically, the electron beam can be focused to a spot with a diameter of $\sim$100 Å on the sample surface, which is the limit of the resolution. The sample need to be conductive and connected with the electrical ground, or electrons will accumulate in the sample. The charged sample will deflect the electrons, resulting in an excessively large spot of electron beam and blurred image. The charging problem for the nonconductive sample can be reduced or eliminated by coating the sample with a thin layer of conductive metal (normally AuPd alloy) or carbon and connecting it to ground using conductive adhesive.
Fig. 3.2 Specimen-electron interaction volume and the secondary products, backscattered electrons, secondary electrons, used for imaging and x-rays for compositional analysis

### 3.2.2 Specimen-Beam Interaction

When an incident electron hits the surface of a sample, it undergoes a series of complex interactions with the nuclei and electrons of the atoms of the sample. The interaction produce a variety of secondary products, such as backscattered electrons (BSE), secondary electrons (SE), X-rays, Auger electrons, and light [54].

When electrons interact with atom in the sample, they experience scattering by the atoms and gradually change directions and lose energy. There is no sharply defined region of scattering. Usually, the volume where interactions are most likely to occur is teardrop shaped, as illustrated in Fig. 3.2. The interaction volume varies with the accelerating voltage and inversely with the atomic number $Z$ of the sample. In other
words, the higher the accelerating voltage or the smaller the atomic number $Z$, the higher the interaction volume.

The interactions between the incident electrons and the atoms the sample can be elastic and inelastic. An important elastic interaction is the one that produces the backscattered electrons (BSE), which are high in energy, with an average of 60% to 80% of the initial energy of the incident electrons. The secondary electrons (SE) are produced from an inelastic interaction between incident electrons and weakly bound conduction band electrons in the atoms of the sample. The average energy of SE is about 3eV to 5eV. Both BSE and SE are produced within the whole interaction area. Because of their different in energy, their escape depths are different. Secondary electrons are strongly absorbed by the sample. Only those produced within ~5 nm in metals and ~50 nm in insulators near the surface can escape and be detected. The escape depth of BSE is a few times larger than that of SE. Thus the SE provides predominantly topographical images, which have the highest resolution. Images from BSE are depth images, which are less sensitive to the surface details than those from SE.

The secondary electron detector shown in Fig. 3.2 collects the secondary electrons emitted from the sample are generated in a signal for display. The display shows a spot with the brightness proportional to the magnitude of the signal, which is proportional to the number of electrons collected by the detector. The scan coils along the path of the incident electrons can generate a variable magnetic field, which deflects the incident electron beam to scan across a certain area on the sample. For each point that the incident electrons bombard, there will be a spot on the display corresponding to that point. Since
the number of secondary electrons emitted from the sample surface is determined by the
morphology and the chemical composition of the area bombarded by the incident
electrons, the display can reveal the surface morphological structure.

3.2.3 Energy Dispersive Spectroscopy (EDS)

Energy dispersive spectroscopy (EDS) is an analytical technique used for the
elemental analysis or chemical characterization of a sample. It is one of the variants of X-
ray fluorescence spectroscopy which relies on the investigation of a sample through
interactions between electromagnetic radiation and matter, analyzing X-rays emitted by
the matter in response to being hit by high energy charged particles. Its characterization
capabilities are due in large part to the fundamental principle that each element has a
unique atomic structure allowing X-rays that are characteristic of an element's atomic
structure to be identified uniquely from one another.
Fig. 3.3 Schematic of EDS mechanism: Some electrons in the inner shells of the atoms in the sample are removed by inelastic scattering and leave holes in the inner shells. When the electrons from outer shells fill the vacancies in the inner shells, the atoms emit x-rays with characteristic energy and wavelength.

EDS is commonly equipped with SEM systems. As illustrated in Fig. 3.3, during specimen-beam interactions, some electrons in the inner shells of the atoms in the sample are removed by inelastic scattering and leave holes in the inner shells. When the electrons from outer shells fill the vacancies in the inner shells, the atoms emit x-rays with characteristic energy and wavelength. Each element has its distinctive spectrum of x-rays, which can be used as a fingerprint to identify the element.

EDS analysis can be performed in an area of various sizes, along a line, across the sample surface, or at a spot, depending on the requirements of the compositional analysis.
3.3 X-Ray Diffraction (XRD)

The discovery of x-rays on 8 November 1895 by Rontgen is a great event in the history of science, and he was awarded the first Nobel Prize in physics in 1901[55]. Since then, x-ray has been widely used in scientific research and medical diagnostics. X-ray diffraction, a result from the interaction between x-ray and materials, gives information about the structure of materials, such as the crystal phase, thickness and roughness of layered structures, grain size of polycrystals, texture and stress of samples, orientation and quality of single crystals, etc.

![Schematic of x-ray diffraction in a crystal lattice with lattice constant d](image)

Fig. 3.4 Schematic of x-ray diffraction in a crystal lattice with lattice constant d

X-rays are electromagnetic waves with wavelength in the range from $10^{-12}$ m to $10^{-9}$ m [56]. When a beam of x-rays interacts with a material with periodicity, such as a
crystal, diffraction can happen if the wavelength of the x-ray is comparable to the lattice constant. A series of diffraction peaks can be detected at specific angles. Each constructive diffraction peak satisfies Bragg's law,

\[ 2d \sin \theta = n\lambda \]  

(3.1)

where \( n \) is the diffraction order, \( \lambda \) is the wavelength of the x-ray, \( d \) is the spacing between atomic planes, and \( 2\theta \) is the angle between the incident and diffracted x-ray beams, as shown in Fig. 3.4. Each material with a particular crystal structure has its distinctive diffraction pattern, which can be used to identify the structure of the material. For example, the cubic structure, which is the most common crystal structure, can be divided into simple cubic (sc), body-centered cubic (bcc), and face-centered cubic (fcc). The distance between two crystallographic planes labeled by Miller indices [57], may be calculated from:

\[ d_{hkl} = \frac{a_o}{\sqrt{h^2+k^2+l^2}} \]  

(3.2)

where \( a_o \) is lattice constant. Since peak position can be determined by Bragg’s equation, we can calculate the theoretical location from the equation:

\[ 2\theta_{hkl} = 2 \sin^{-1} \frac{\lambda\sqrt{h^2+k^2+l^2}}{2a_o} \]  

(3.3)

The intensity of diffracted beam is related to an imaginary function, known as structure factor

\[ I_{hkl} \propto |F_{hkl}|^2 \]  

(3.4)

The structure factor depends on the type of atoms and their position within a unit cell. It is expressed as a sum of all atoms in the crystal

\[ F_{hkl} \propto \left( \sum f_i i \sin[2\pi(hx_i + ky_i + lz_i)] + \sum f_i i \cos[2\pi(hx_i + ky_i + lz_i)] \right) \]  

(3.5)
where \( f_i \) is a scattering factor for atom \( i \) and it is related to its atomic number. The structure factor depends on the type of atoms and their position within a unit cell.

The typical X-ray diffraction pattern contains a lot of information. From peak position we may determine the space group symmetry, translational symmetry, unit cell dimension, and make qualitative phase identification. Intensity of the peak may help us to uncover unit cell contents and find the point symmetry. We may also calculate crystal size, non-uniform micro-strain, and specify extended defects, such as stacking faults, twins, or anti-phase boundaries.

### 3.4 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.
3.4.1 Fundamentals of TEM

A TEM is basically composed of several components: 1) a vacuum system in which the electrons travel; 2) an electron emission source for generation of the electron stream; 3) a series of electromagnetic lenses and electrostatic apertures, which allow the
operator to guide and manipulate the beam; 4) a sample stage, which allows the insertion into, motion within, and removal of specimens from the beam path; 4) and an imaging system [59].

Imaging methods in TEM utilize the information contained in the electron waves exiting from the sample to form an image. The projector lenses allow for the correct positioning of this electron wave distribution onto the viewing system. The observed intensity of the image $I$, assuming sufficiently high quality of the imaging device, can be approximated as proportional to the time-average amplitude of the electron wave functions

$$I(x) = \frac{k}{t_1 - t_0} \int_{t_0}^{t_1} \Psi \Psi^* \, dt$$  \hspace{1cm} (3.6)

where $\Psi$ is the wave function of the exit beam [60].

Different imaging methods therefore attempt to modify the electron waves exiting the sample in a form that is useful to obtain information with regards to the sample, or beam itself. As seen in Equation 3.6, it can be deduced that the observed image depends not only on the amplitude of beam, but also on the phase of the electrons.

### 3.4.2 Resolution and Contrast of TEM

TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons [58]. Theoretically,
the maximum resolution, d, that one can obtain with a light microscope has been limited by the wavelength of the photons λ and the numerical aperture of the system NA:

\[ d = \frac{\lambda}{2n \sin \theta} \approx \frac{\lambda}{2NA} \quad (3.7) \]

While de Broglie wavelength of electrons can be express as:

\[ \lambda_e \approx \frac{h}{\sqrt{2m_0E(1+\frac{E}{2m_0c^2})}} \quad (3.8) \]

where h is Planck's constant, \( m_0 \) is the rest mass of an electron and E is the energy of the accelerated electron. By accelerating electrons to a few hundred keV, a TEM can provide high resolution up to Å scale [59].

Compared with SEM, a TEM can provide higher resolution imaging (0.1 nm) because it utilizes elastic scattering. This is an interaction process that is highly localized to the region occupied by the screened Coulomb potential of an atomic nucleus, whereas SEM utilizes the inelastic scattering that is more diffuse and spreads out over a nanometer. The TEM works in a way that the sources of the electron beam is at the top of a thin specimen and the recording system is at the bottom the specimen. In a conventional TEM, a beam of high-energy electrons (typically 100 - 400 keV), emitted from an electron gun if focused by a two or three stage electromagnetic condenser-lens system, which permits variation of the illumination aperture and the area of the illuminated specimen. The focused electron beam strikes the specimen and the transmitted or scattered electron-intensity distribution behind the specimen is imaged with an multi-stage objective lens system onto a fluorescent screen or CCD or digital-image recording.
For the case of a fluorescent screen, the image is recorded by direct exposure of photographic emulsion inside the vacuum.

In high resolution TEM (HRTEM), instead of recording amplitude of diffracted electron wave function, the phase of the diffracted wave is preserved and interferes constructively and destructively with the phase of transmitted wave. The technique of phase contrast imaging is used to obtain images of column of atoms in a specimen.

In a TEM measurement, electrons interact strongly with sample atoms by elastic and inelastic scattering. Therefore in order to make sure high-energy electrons pass through the sample for imaging or electron-diffraction pattern, the sample are required to be thin, typically of the order of 5nm ~500nm for 100 keV electrons, depending on the density and elemental composition of the object and the resolution desired.

The two common imaging techniques in TEM are conventional imaging and high-resolution imaging (phase contrast imaging). In conventional imaging, an image is typically formed by utilizing either un-scattered electrons, elastically scattered electrons, or a combination of them. In general, conventional imaging can be obtained through two modes: bright-field (BF) and dark-field (DF). BF and DF images are obtained by selecting two different types of electrons through positioning of an objective aperture at a specific location in the back focal plane of objective lens in the TEM. A BF image is formed by selecting only the un-diffracted electrons (incident electrons that are transmitted through the thin specimen), while DF images is formed by selecting only some diffracted electrons.
In conventional TEM studies of crystalline crystals, features in the image mainly come from diffraction contrast that is the variation in the intensity of electron diffraction across the specimen, which is observed by using the objective aperture. Diffraction contrast is particularly useful for imaging grain structures and identifying defects such as dislocations, twins, and interfaces. The features in the diffraction contrast imaging are much clearer than that for the imaging without using an objective aperture. The reason for this difference is that without the objective aperture, the interference of the diffracted and transmitted intensity suppresses the observed diffraction contrast. In the aperture-less case, besides diffraction contrast, other contrast mechanism also exists, that is, mass-thickness contrast. Mass-thickness contrast arises from incoherent and elastic scattering, which increases with the atomic number and the thickness of the specimen. Therefore, mass-thickness contrast can be useful for identifying the variations in composition and thickness in the specimen.

3.5 Photoluminescence Spectroscopy

Photoluminescence spectroscopy (PL) is a process in which a substance absorbs photons and then re-radiates photons. Excitation to a higher energy state is triggered and then those electrons return to a lower energy state accompanied by the emission of photons. It is a non-destructive technique which investigates the electronic structure around and below the energy gap of semiconductor materials. It is widely used for characterization of direct-band gap semiconductors [61-63].
Fig. 3.6 General steps involved in a PL experiment.

PL can be defined as an optical excitation-emission process, in which photons of $h\nu > E_g$ are absorbed by the semiconductor, creating electron-hole (e-h) pairs that subsequently will recombine and emit photons. The steps involved in the general PL process are schematically represented in Fig. 3.6. (1) The e-h pair excitation: Initially, the e-h pairs are photo-excited to a non-equilibrium state by absorption of light (generally, generated by a laser). (2) The e-h pair thermalization and diffusion: The e-h pairs diffuse and relax into a quasi-equilibrium distribution to the lowest energy state (non-radiative process). (3) The e-h recombination: The e-h pairs recombine, emitting photons or by other non-radiative processes. Different from the direct-band semiconductors, in indirect-band semiconductors, the minimum of the conduction band does not coincide in momentum space with the maximum of the valence band. A similar situation, called “spatially indirect bandgap” structure, arises when the electrons are confined in one material and the holes are confined in a different material. This gives rise to a difference...
between the absorption energy and the emission energy, as well as a longer time to
diffuse and relax, hereby leading a less probability of the last step (3) than the direction
transition. This indirect alignment could be a potential advantageous structure in the
study of spin relaxation time.

Photoluminescence is commonly used in labs and semiconductor industry due to
its advantages: (1) characterization of the most fundamental optical properties of the
grown materials, such as band gap, donor and/or acceptor states, deep defect levels, the
quality and the band structure of epilayers; (2) It is a non-destructive technique where
only small quantities of material are needed. (3) It provides information mainly on
minority carrier properties and, thus, it is complementary to electrical characterization
techniques. The lifetime, the diffusion length, the quantum efficiency could be inferred
through the study of the recombination paths. When the photo-generated $e-h$ pair density
is larger than the free carrier concentration (high excitation conditions), majority carrier
properties are also accessible. (4) It is an easy technique because it does not require
particular sample handling and preparation. The experimental set-up complexity is
proportional to the needs: for fast characterization a very simple and inexpensive
apparatus is adequate. (5) It is sensitive to the chemical species of impurities, which can
be detected even at very low densities. (6) It is an optical spectroscopic technique, i.e., it
gives energetically resolved information.
Chapter 4

Growth control of GaAs nanowires using pulsed laser deposition with arsenic over-pressure

4.1 Fundamentals of GaAs nanowires

4.1.1 General properties of GaAs

Gallium Arsenide (GaAs) is a direct-band gap III-V compound semiconductor crystal. It has been widely used in the manufacturing of devices such as microwave frequency integrated circuits, monolithic microwave integrated circuits, infrared light-emitting diodes, laser diodes, solar cells, and optical windows [64-66].

Fig. 4.1 Unit Cube Cell of GaAs crystal. Ga atoms are colored in black while P atoms are colored in white
GaAs nanowires have the same zinc-blende (ZB) crystal as bulk GaAs. In zinc-blende GaAs nanowires, the space lattice is face-centered cubic (FCC) with a basis of two atoms (one Ga and one As). The lattice can be viewed as two FCC lattices separated by 1/4 of the body diagonal of the unit cube. One lattice is occupied by Ga atoms, and the other by As atoms. Each atom has 4 nearest neighbors of the opposite kind and is bound to these 4 atoms which are arranged at the corners of the surrounding tetrahedron. The bonding is mainly covalent. The crystal structure of GaAs crystal is shown below in Fig. 4.1. Other important physical properties of GaAs at room temperature are shown in Table 4.1.
<table>
<thead>
<tr>
<th>Properties</th>
<th>Parameter Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
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<td>Lattice constant</td>
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<tr>
<td>Density</td>
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<td>Atomic density</td>
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<tr>
<td>Molecular weight</td>
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<tr>
<td>Bulk modulus</td>
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<tr>
<td>Sheer modulus</td>
<td>$3.26 \times 10^{11}$ dyn/cm²</td>
</tr>
<tr>
<td>Coefficient of thermal expansion</td>
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</tr>
<tr>
<td>Specific heat</td>
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<tr>
<td>Lattice thermal conductivity</td>
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<td>Hole mobility</td>
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</tr>
<tr>
<td>Melting point</td>
<td>1238°C</td>
</tr>
</tbody>
</table>

Table 4.1 Physical properties of GaAs bulk at room temperature

GaAs is a direct band-gap semiconductor, which means that the minimum of the conduction band is directly over the maximum of the valance band (Fig. 3.3). Transitions between the valance band and the conduction band require only a change in energy, and no change in momentum, unlike indirect band-gap semiconductors such as silicon. This property makes GaAs a very useful material for manufacturing light-emitting diodes and semiconductor lasers, since a photon is emitted when an electron changes energy levels from the conduction band to the valance band. Alternatively, an incident photon can
excite an electron from the valence band to the conduction band, allowing GaAs to be used in photo detectors [67].

![Graph showing band gap structure of Si and GaAs]

**Fig.4.4 Band Gap Structure of Si (Left) and GaAs (Right) [67]**

GaAs has a higher saturated electron velocity and higher electron mobility than silicon, allowing transistors made from it to function at frequencies in excess of 250 GHz. Unlike silicon junctions, GaAs devices are relatively insensitive to heat. Also, GaAs devices generate less noise than silicon devices when operated at high frequencies. They can also be operated at higher power levels than the equivalent silicon device because they have higher breakdown voltages. These properties recommend GaAs circuitry in mobile phones, satellite communications, microwave point-to-point links, and some radar systems. It is used in the manufacture of Gunn diodes for generation of microwaves.
Because of its wide bandgap, pure GaAs is highly resistive. Combined with the high dielectric constant, this property makes GaAs a very good electrical substrate and unlike Si provides natural isolation between devices and circuits. This has made it an ideal material for microwave and millimeter wave integrated circuits, MMICs, where active and essential passive components can readily be produced on a single slice of GaAs.

GaAs has three major disadvantages over Silicon in integrated circuit fabrication. (1) Silicon is abundant and cheap to process. Si is highly abundant in the Earth's crust, in the form of silicate minerals. The economy of scale available to the silicon industry has also reduced the adoption of GaAs. In addition, Si crystal has an extremely stable structure mechanically and it can be grown to very large diameter boules and can be processed with very high yields. It is also a decent thermal conductor thus enable very dense packing of transistors, all very desirable for design and manufacturing of very large ICs. (2) Silicon dioxide is one of the best insulator which can be easily be incorporated onto silicon circuits, and such layers are adherent to the underlying Si. While GaAs does not easily form such a stable adherent insulating layer and does not have stable oxide either. (3) Silicon possesses a much higher hole mobility. This high mobility allows the fabrication of higher-speed P-channel field effect transistors, which are required for CMOS logic. Because they lack a fast CMOS structure, GaAs logic circuits have much higher power consumption, which has made them unable to compete with silicon logic circuits [68].
4.1.2 GaAs nanowire growth mechanism

A typical VLS process starts with the dissolution of gaseous reactants into nanometer-sized liquid droplets of a catalyst, followed by nucleation and growth of single-crystal wires. The 1D growth is induced and dictated by the liquid droplets, whose sizes remain essentially unchanged during the entire process of wire growth. Each liquid droplet serves as a soft template to strictly limit the lateral growth of an individual wire.

All major steps involved in a VLS process are illustrated in Fig. 1a, with the growth of GaAs Nanowire [26]. Based on GaAs-Au phase diagram as shown in Fig. 4.3 (a), GaAs and Au form liquid alloy when the temperature is above eutectic point 630 °C. Once the liquid droplet is supersaturated with GaAs, nanowire growth will start to occur at solid-liquid interface. The establishment of the symmetry-breaking solid-liquid interface is the key step for the one-dimensional nanocrystal growth in this process.
4.1.3 Motivation of arsenic over-pressure

Most GaAs nanowires have been synthesized via VLS mechanism by pulsed laser deposition [69-72], molecular beam epitaxy (MBE) [73-76] or metal–organic vapor phase epitaxy (MOVPE) [72, 77-81]. MBE and MOVPE typically produce GaAs nanowires with tapered shape and length of 1–2 μm long, with a few exceptions up to ~8 μm long. The short length makes it challenging for the fabrication of electrical contacts on
individual nanowires and the tapered shape complicates electronic characterization. PLD has advantages in the synthesis of semiconductor nanowires with uniform diameter and length up to tens of micrometers. However, it is well known that arsenic is highly volatile and tends to escape from the GaAs surface at the GaAs growth temperature. To overcome this problem, arsenic over-pressure with considerable As/Ga flux ratio is provided to grow stoichiometric GaAs in MBE and MOVPE [76, 78]. Typical PLD systems do not have the capability to supply arsenic over-pressure. To our knowledge, there has been no report on controlling GaAs nanowire growth by PLD with arsenic over-pressure. In this work, the author introduced an additional arsenic source in the PLD system in order to obtain stoichiometric growth of GaAs nanowires.

4.2 Experiment Details

Fig. 4.4 Schematic of the PLD system with an in situ transfer assembly to provide arsenic over-pressure: The standby position is the location of the arsenic source during the temperature ramp up of the furnace. The transfer assembly is slid by the magnet to the growth position shortly before the nanowire synthesis.
GaAs nanowires were fabricated using a PLD system comprised of a KrF excimer laser and a quartz tube furnace, as schematically shown in Fig. 4.4. A pressed target made from GaAs polycrystalline powders is positioned 1 inch outside the upstream end of the furnace. Monodisperse Au nanoparticles with nominal diameter of 50 nm are dispersed onto thermally oxidized Si substrates which are then loaded in the quartz tube between the center and the downstream end of the furnace. The quartz tube is evacuated by a mechanical pump to a base pressure below 5 mTorr before the furnace starts to heat up. The temperature at the center of the furnace, $T_{\text{center}}$, is controlled at between 750 and 1000 $^\circ$C. The location of the substrate is typically 8–9 inches from the center of the furnace on the downstream side, giving a growth temperature of the substrate, $T_{\text{sub}}$, between 570 and 650 $^\circ$C. Once the growth temperature is reached, an argon flow of 80 sccm is sent in with the pressure in the quartz tube controlled at 200 Torr. Then, a 10 Hz pulsed laser beam with a wavelength of 248 nm and duration of 10 ns is focused into a $2.5 \times 3.5$ mm$^2$ spot on the GaAs target to start the ablation which produces Ga and As vapors. The laser energy density is maintained at 1.2–1.3 J cm$^{-2}$ per pulse on the target.

During the initial stage of the laser ablation on a new GaAs target, the amount of As vapor generated is more than that of Ga vapor because As is more volatile than Ga. The extra loss of As relative to Ga from the target leaves more Ga than As on the surface of the target, which leads to less As and more Ga vapor generated by the ablation with time. Eventually, equilibrium is reached and the laser ablation on the ‘mature’ GaAs target generates equal amounts of Ga and As vapors. The ‘maturation’ of the target takes a few minutes as the material loss on the surface of the target is obvious. All the nanowires growth in this work used mature targets so that the amounts of Ga and As
vapors generated by laser ablation are equal. The temperature of the GaAs during the whole process was kept under 100 °C, at which the decomposition of GaAs is negligible.

After the nanowire growth for 20 min, the furnace top was immediately opened and the quartz tube was cooled down quickly by a fan. Field-emission scanning electron microscopy (SEM), high resolution TEM, energy-dispersive spectroscopy (EDS) and x-ray diffraction were used to characterize the structure and composition of the GaAs nanowires. To prepare the samples for TEM measurements, substrates with nanowires were sonicated in ethanol to make suspensions of nanowires. Then a drop of the suspension was dispersed onto the TEM grids.
4.3 Experiment Results

4.3.1 Problems with conventional PLD GaAs nanowire growth

Fig. 4.5  SEM images of GaAs nanowires (a) at low magnification, (b) grown at $T_{\text{center}} = 750 \, ^\circ\text{C}$ and $T_{\text{sub}} = 640 \, ^\circ\text{C}$ without As$_2$ over-pressure, (c) grown at $T_{\text{center}} = 750 \, ^\circ\text{C}$ and $T_{\text{sub}} = 610 \, ^\circ\text{C}$ without As$_2$ over-pressure, (d) grown at $T_{\text{center}} = 1000 \, ^\circ\text{C}$ and $T_{\text{sub}} = 640 \, ^\circ\text{C}$ with As$_2$ over-pressure, (e) grown at $T_{\text{center}} = 880 \, ^\circ\text{C}$ and $T_{\text{sub}} = 640 \, ^\circ\text{C}$ with As$_2$ over-pressure, and (f) grown at $T_{\text{center}} = 880 \, ^\circ\text{C}$ and $T_{\text{sub}} = 570 \, ^\circ\text{C}$ with As$_2$ over-pressure. The insets in (b), (c) and (f) are higher-magnification images of the respective figures.
GaAs nanowires were first synthesized at $T_{\text{center}} = 750 \, ^\circ\text{C}$ and $T_{\text{sub}}$ from 570 to 650 $^\circ\text{C}$ without arsenic over-pressure. The low-resolution SEM image in Fig. 4.5 shows GaAs nanowires with lengths up to 100 $\mu\text{m}$. However, a closer look at high magnification reveals subtle details of the nanowires, as shown in Fig. 4.5 (b) and (c) for nanowires grown at $T_{\text{sub}} = 640 \, ^\circ\text{C}$ and 610 $^\circ\text{C}$, respectively. Although some nanowires have uniform diameters of $\sim 50$ nm and clean surface, many nanowires deviate from cylindrical wire geometry. At $T_{\text{sub}} = 640 \, ^\circ\text{C}$, many nanowires have rough surfaces and kinks with diameters considerably larger than 50 nm, as shown in the inset of Fig. 4.5 (b), while at $T_{\text{sub}} = 610 \, ^\circ\text{C}$, the nanowires are typically $\sim 50$ nm in diameter, but with many dust-like particles attached to them (inset of Fig 4.5(c)).

Fig. 4.6 (a) shows a TEM image of such a dusty GaAs nanowire which exhibits crystalline facets on these particles attached to the nanowire. A high-resolution TEM image over an area indicated by the white box in Fig. 4.6 (a) near the interface between a particle (right) and the nanowire (left) is shown in Fig. 4.6 (b). Both the nanowire and the particle are single crystals with clear atomic planes. However, they do not have the same orientation, i.e., there is no epitaxy between them. The orientation of the TEM sample was adjusted to align the zone axis along the $[\bar{1}11]$ direction of the particle, as verified by the Fourier transformation pattern (Fig 4.6(c)) taken within the dashed white box in Fig 4.6 (b). The pair of white lines in the particle indicate the (220) atomic planes with a spacing of $2.0 \, \text{Å}$. Meanwhile, the nanowire section of Fig 4.6 (b) is not along any crystal orientation and its Fourier transformation pattern is difficult to recognize.
Fig.4.6 (a) TEM image of a GaAs nanowire grown at $T_{\text{center}} = 750 \, ^\circ\text{C}$ and $T_{\text{sub}} = 610 \, ^\circ\text{C}$ without $\text{As}_2$ over-pressure at medium magnification and (b) high-resolution TEM image over an area marked by the white box in (a) near the interface between the nanowire (left) and a particle (right). The two white lines inside the particle label the (220) planes with a spacing of 2.0 Å. The arrow points along the nanowire axis. (c) The Fourier transformation pattern over the area of the dashed box in (b) confirms the orientation of the particle (zone axis along $[\bar{1}11]$). (d) The EDS spectrum taken near the area of (b) gives an atomic ratio $\text{Ga:As:O} = 1.49:1.00:0.24$, suggesting that the amorphous material in between the nanowire and the particle is a mixture of Ga metal and gallium oxides.
There is a layer of ~5 nm thick amorphous material in between the particle and the nanowire in Fig. 4.6 (b). Chemical composition analysis from the EDS spectrum (Fig. 4.6 (d)) taken over the area of Fig. 4.6 (b) gives an atomic ratio Ga:As:O = 1.49:1.00:0.24. We believe the extra Ga comes from the amorphous material. It is well known that the surface of GaAs nanowires has a layer of gallium oxide. Assuming all the O is from Ga₂O₃, the most stable phase of gallium oxide, there is 16% Ga in the form of Ga₂O₃ and 33% metallic Ga relative to the amount of stoichiometric GaAs in the nanowire and the particle. It is possible that the amorphous material is a mixture of metallic Ga, Ga₂O₃ and other forms of oxides such as Ga₂O.

We attribute the non-ideal geometries of the GaAs nanowires and the extra Ga to the loss of arsenic from the GaAs nanowires during the growth. At growth temperatures of 570–640 °C, arsenic in the just-grown GaAs nanowires tends to escape from the nanowires under equal Ga and As partial pressure generated by the laser ablation, leaving Ga on the nanowire surface. The metallic Ga on the nanowire surface serves as a catalyst, just like the Au nanoparticles, and absorbs Ga and As vapors to initiate additional GaAs growth. At T_{sub} = 640 °C, metallic Ga remains spreading on the nanowire surface and catalyzes GaAs layer growth on the existing GaAs nanowire surface, resulting in much thicker GaAs nanowires. While the large thickness of the nanowires in Fig. 4.5 (b) prohibits high-resolution TEM study of the atomic structure, EDS analysis on these thick nanowires reveals more Ga than As, similar to that in Fig 4.6 (d). As substrate temperature decreases to T_{sub} = 610 °C, metallic Ga beads up to form nanodroplets on the GaAs nanowires. Some of the Ga beads catalyze additional GaAs growth, producing GaAs particles on the GaAs nanowires, such as those shown in Fig. 4.6 (a) and (b).
Because the nucleation of the GaAs particle starts from Ga beads and the crystalline particles typically do not see the crystalline nanowire, there is no epitaxial relationship between the particles and the nanowire that they grow on. The metallic Ga on the nanowire surface gets partially oxidized when exposed to air, forming the surface oxides.

4.3.2 Arsenic over pressure for PLD GaAs NW growth

A different approach to arsenic over-pressure is to heat an arsenic source using the furnace. Because it takes the furnace over an hour to reach the set temperature of 750–1000 °C, the arsenic source cannot be loaded into the furnace before heating. Otherwise, the slow heating process leads to uncontrollable arsenic vapor and contamination of the substrate. In order to overcome this problem, we incorporated an in situ transfer device as shown in Fig. 4.4 to move the arsenic source into and out of the furnace without breaking the vacuum at high temperatures. The transfer device is an assembly consisting of a piece of soft Fe, a 12 inch long ceramic rod and a ceramic plate. The arsenic source is put in a ceramic cell on the ceramic plate and a magnet can slide the soft Fe inside the quartz tube. The transfer assembly is positioned outside the furnace during the temperature ramp up, as illustrated by the dark transfer assembly labeled standby position in Fig. 4.4. The temperature of the arsenic source at the standby position is under 100 °C. The arsenic source is inserted into the center of the furnace 10 min before the start of nanowire growth, as indicated by the gray transfer assembly in Fig. 4.4.

We first used arsenic powders to generate arsenic vapor by sublimation at various furnace temperatures. However, the side growth on GaAs nanowires persists, resulting in
similar shapes as those shown in Fig. 4.5 (b) and (c). Obviously, the arsenic vapor generated by sublimation did not compensate for the loss of arsenic from the nanowire surface. This is due to that the sublimation of arsenic produces $\text{As}_4$ molecules. It is well known from the GaAs growth by MBE that $\text{As}_4$ molecules require a fairly high energy to break into As atoms which are required to form GaAs. Since $\text{As}_2$ molecules are much easier to break, most MBE systems use an arsenic cracker to break $\text{As}_4$ molecules into $\text{As}_2$ molecules in order to grow GaAs [74-76]. If an $\text{As}_2$ over-pressure can be provided during GaAs nanowire growth, the abundant $\text{As}_2$ molecules cover the GaAs nanowire surface and can easily break into As atoms to compensate for the loss of arsenic and maintain stoichiometric GaAs nanowires. In the presence of $\text{As}_4$ overpressure, although $\text{As}_4$ molecules cover the nanowire surface, they cannot break into As atoms easily to compensate for the loss of arsenic.
Fig. 4.7 (a) TEM image of a GaAs nanowire grown at $T_{\text{center}} = 880$ °C and $T_{\text{sub}} = 570$ °C with As$_2$ over-pressure at medium magnification (inset: the end of a nanowire with a Au cap), (b) high-resolution TEM image inside the nanowire with the zone axis along the [11$\bar{2}$] direction (inset: Fourier transformation pattern), and (c) high-resolution TEM image at the surface of the nanowire. The ‘ripples’ near the nanowire surface are an instrumental artifact due to the diffraction of the electron beam at high magnification. The two white boxes in (a) mark the areas where (b) and (c) were taken. The surface oxide layer is less than 1 nm thick. (d) The EDS spectrum taken over the nanowire gives an atomic ratio Ga:As = 1.04:1.00. The extra Ga is from the thin surface oxide layer.
Since an arsenic cracker is not practical for PLD systems, we took a different route to generate $\text{As}_2$ vapor by thermal decomposition of polycrystalline GaAs, which releases $\text{As}_2$ molecules, using the in situ transfer device described above[82]. Fig. 4.5(d) shows the SEM image of the GaAs nanowires grown at $T_{\text{center}} = 1000 \, ^\circ\text{C}$ and $T_{\text{sub}} = 640 \, ^\circ\text{C}$ with $\text{As}_2$ over-pressure. There are some large structures of a few micrometers on some nanowires. These are GaAs crystals originated from epitaxial growth of GaAs on the side of some part of the nanowires in high $\text{As}_2$ over-pressure at $T_{\text{center}} = 1000 \, ^\circ\text{C}$, which should be distinguished from the Ga catalyzed growth as shown in Fig. 4.5 (b) and (c). The epitaxial growth of GaAs on nanowires is similar to the deposition of GaAs films by MBE, which requires high $\text{As}_2$ over-pressure to cover the GaAs surface with As for subsequent GaAs growth [82]. For nanowire growth, it is desirable to maintain an $\text{As}_2$ overpressure at a level that it just compensates for the loss of As from the nanowires, but not enough to cover the nanowire surface with As for epitaxial growth. This optimal condition can be achieved by lowering the $\text{As}_2$ partial pressure at lower $T_{\text{center}}$. The SEM image of GaAs nanowires grown at $T_{\text{center}} = 880 \, ^\circ\text{C}$ and $T_{\text{sub}} = 640 \, ^\circ\text{C}$, as shown in Fig 4.5(e), exhibits long nanowires with uniform diameter and no side growth of GaAs. However, they typically have zigzags because the substrate temperature is too high and the nanowires change growth directions.

At $T_{\text{sub}} = 570 \, ^\circ\text{C}$ and $T_{\text{center}} = 880 \, ^\circ\text{C}$, we obtained straight GaAs nanowires with uniform diameter of $\sim 50 \, \text{nm}$ and length over $20 \, \mu\text{m}$, as shown in Fig. 4.5 (f). The kinks in a small number of nanowires suggest that some defects still exist under this condition. Further optimization should be able to reduce the defects in the nanowires. A TEM image of one such GaAs nanowire is shown in Fig. 4.7(a) with a uniform diameter of $50 \, \text{nm}$ and
smooth surface. High-resolution TEM image inside the nanowire in Fig. 4.7 (b) shows two perpendicular atomic planes of (111) and (220) with a spacing of 3.3 Å and 2.0 Å, respectively, as indicated by the two pairs of white lines. The Fourier transformation pattern in the inset of Fig. 4.7 (b) with the zone axis along [11\(\bar{2}\)] confirms the atomic planes.

The TEM image near the surface of the nanowire shown in Fig. 4.7 (c) reveals that the nanowire axis is along the [111] direction as indicated by the white lines highlighting the (111) planes. The surface oxide layer is estimated to be no more than 1 nm thick. The ‘ripples’ near the nanowire surface are an instrumental artifact due to the diffraction of the electron beam at high magnification, which is most visible near the outside of the object edges. The thin surface oxide layer is further supported by the EDS analysis (Fig. 4.7(d)) on the nanowire, which gives an atomic ratio Ga:As = 1.04:1.00. The relatively high intensity of the O peak in Fig. 4.7 (d) is most likely due to contamination by the organic solvent used to prepare the TEM sample. Assuming the single-crystal GaAs within the nanowire is stoichiometric, the extra 4% Ga should be from the surface. This corresponds to a single-crystal core of GaAs with a diameter of 49 nm and a surface gallium oxide layer of 0.5 nm thick, which gives a total diameter of 50 nm for the nanowire. This thin surface oxide layer is the result of appropriate As\(_2\) over-pressure and the quick cool down right after the nanowire growth which minimizes the thermal decomposition of the nanowires.

We also used x-ray diffraction to verify the crystal structure of the nanowires grown at \(T_{\text{sub}} = 570^\circ\text{C}\) and \(T_{\text{center}} = 880^\circ\text{C}\) such as those shown in Fig. 4.5 (f) and Fig. 4.7. The \(\theta-2\theta\) scan in figure 5 gives only one GaAs peak, (111), at \(2\theta = 27.3^\circ\), which is the
strongest peak in the powder x-ray diffraction pattern for zinc-blende GaAs. We could not detect other x-ray diffraction peaks because the amount of GaAs in the nanowire sample is very small for the purposes of x-ray diffraction. The peak near 33° is from the Si substrate.

Fig. 4.8 X-ray diffraction of a GaAs sample synthesized at T_{center} = 880 °C and T_{sub} = 570 °C with As$_2$ over-pressure, the same as that shown in Fig. 4.5(f) and Fig. 4.7. Only one GaAs peak is detected because of the small amount of GaAs for x-ray diffraction.

The high crystalline quality and thin surface oxide layer of the nanowires in Fig. 4.5(f) and Fig. 4.7 are desirable for electronic characterization. In order to make electrical contacts with an individual GaAs nanowire, low density 50 nm Au nanoparticles were first dispersed onto a thermally oxidized Si substrate with predefined Ta$_2$O$_5$ markers (for e-beam lithography), followed by the synthesis of n-doped GaAs nanowires using a GaAs target with 0.5% (atomic) Te. The growth conditions were the same as those for the
nanowires in Fig. 4.5(f). While the Ta₂O₅ markers were intact during the growth, they provided sufficient contrast for subsequent nanowire locating during e-beam lithography to define the patterns for electrical contacts. Ni/Au bilayers were deposited by sputtering onto the e-beam patterns. After lift-off, a single nanowire with two electrical contacts is obtained, as shown in the inset of Fig. 4.9. Compared with the common procedure for the fabrication of electrical contacts on individual nanowires using sonication to make a nanowire suspension and dispersion of the nanowire suspension onto a different substrate [71], this fabrication process is gentler to the nanowires. A simple electrical measurement in Fig. 4.9 gives a linear I–V curve with a resistance of 820 Ω which is a reasonable value for a 50 nm nanowire without efforts to make low-resistive ohmic contacts. This high resistance is largely due to the contact resistance and can be greatly reduced by using different metals and thermal treatment, which requires further investigation.

Fig. 4.9 I–V curve of an n-GaAs nanowire with two metallic Ni/Au contacts. Inset: SEM image of the nanowire with electrical contacts. The nanowire diameter is 50 nm and the separation between the two contacts is 6 μm.
4.4 Conclusion

We have systematically studied the synthesis conditions for GaAs nanowires using PLD with various arsenic overpressures. Arsenic over-pressure with As$_2$ molecules is introduced into the system by thermal decomposition of polycrystalline GaAs. Long single-crystal GaAs nanowires with uniform diameter, small diameter distribution and thin surface oxide layer were obtained. A preliminary electrical characterization on an individual GaAs nanowire gives a linear I–V curve with a reasonable resistance. This may lead to more thorough electrical characterization on GaAs nanowires and GaAs nanowire device fabrication.
Chapter 5

Synthesis of epitaxial silicon nanowires on Si (111) substrates
using ultrahigh vacuum magnetron sputtering

5.1 Introduction

5.1.1 Structure and electric properties of Bulk Silicon

Silicon is the most important material in the semiconductor industry because its desirable properties for device applications include superior interface properties with SiO$_2$, high volume manufacturing capability, and controllable electrical properties using doping process. It is the second most abundant element on the earth, always appears in the form of compounds, most often as silica [66, 67].

Silicon, similar to other group IV semiconductors, has the diamond cubic lattice structure with a lattice constant of 5.43 Å. Fig. 5.1 shows the crystalline structure of silicon.
A silicon atom has 14 electrons. When silicon atoms are brought together to form a crystal, the discrete levels are broadened into bands so that all the electros originally in a given energy state have energies slightly different from each other. In crystal, the 3s and 3p states intermingle to form two band separated by a large energy gap with forbidden energy state. Fig. 5.2 is the electron band gap structure of silicon. In this figure, Energy (E) versus wave vector (k) (or crystal momentum P) relationship is plotted. The maximum in the valence band energy occurs at k=0. However, the minimum in the conduction band energy does not occur at k=0, but along the [100] direction. The difference between minimum conduction band energy and maximum valence band energy in defined as the band gap energy (E_g). A semiconductor whose maximum valence band and minimum conduction band energies do not occur at the same k-value is called an indirect bandgap semiconductor. Due to its very low quantum efficiency, silicon in its bulk form is far from the attractive materials for optoelectronic applications [67].
The electrical properties of silicon can be adjusted by dopants. Phosphorus belongs to group V elements and has five valence electrons. If one phosphorus atom replaced a silicon atom, four valence electrons contribute to bond and one excess electron forms. Because the fifth electron is not a part of the valence bond structure, the energy required to liberate this electron is much lower than that required to break a valence bond. This type of dopant is called a donor and makes the electron a majority carrier. On the other hand, if a group III atom such as boron replaces silicon, the impurity atoms contribute only three valence electrons. Those three electrons form valence bonds with neighboring silicon atoms. In the fourth bond there is missing electrons, which forms a so called hole. An electron from neighboring bond may move in to this hole with very little expenditure of energy, leaving a hole behind. This type of dopant is called an acceptor and makes the hole majority carrier.
Important physical properties of Si at room temperature are shown in Table 5.1.

<table>
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<th>Parameter Values</th>
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</tr>
<tr>
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</tr>
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</table>

Table 5.1 Important physical properties of Si at room temperature

5.1.2 Possibility of silicon nanowires application in industry

Si NWs are particularly attractive and promising due to the central role of silicon in the semiconductor industry, which would allow Si nanowires to be implemented using existing technologies and equipments. The inherently small size of Si NWs allows device...
fabrication with extremely high density and the high surface to volume ratio offers high sensitivity. Si NWs also offer an ideal basis to study the effects of quantum confinement and its possible applications because the bulk properties of silicon are well understood [83, 84]. The carrier types and concentrations in crystalline Si NWs could be controlled by doping, as in bulk Si[84]. In addition, at nanoscale, the motion of carriers in Si NWs could be confined, causing a possible transformation of the electronic band structure from indirect band gap to direct band gap[85, 86], so Si NWs may emit visible light. More importantly, if such nanowires can be ordered and assembled into an appropriate architectural environment, then a host of nano-electronic applications can be envisioned. It has been suggested that Si NWs might be used for developing 1-D high-performance field effect transistors[87] and bio/chemical sensors[88] with extremely low power consumption[89]. Si NWs can also be used to make single-electron transistors (SETs) [90, 91]. They, therefore, can be used to determine the relationship between wire sizes and the electrical characteristics of SETs, which can significantly shorten the development time required to make SET practical devices. Si nanowire based electronics, including field-effect transistors, logic gates, and light-emitting diodes in combination with direct band gap semiconductor nanowires, exhibits outstanding performance and potential for the next generation technological applications.

5.1.3 Motivation of Si NW with sputtering

Most Si nanowires are synthesized by pulsed laser deposition (PLD) or chemical vapor deposition (CVD) using Au nanoparticles as catalysts via vapor-liquid-solid (VLS)
We report an alternative approach to synthesize epitaxial Si nanowires on Si (111) substrates and non-epitaxial Si nanowires on Si (100) substrates with a thermal oxide layer using ultrahigh vacuum (UHV) radio-frequency (RF) magnetron sputtering. Significant differences in the nanowire morphology between the non-epitaxial and epitaxial nanowires were observed [89, 95]. The UHV environment during the nanowire growth provides the capability to minimize the impurity level in the Si nanowires and oxidation on the surface of the Si nanowires, which becomes important as the diameter of the nanowires is reduced.

5.2 Experiment Details

As shown in Fig. 5.3, the UHV magnetron sputter system is equipped with a load lock chamber and two substrate heaters capable of controlling the substrate temperature up to 850 °C with the fluctuation of ±1 °C. The main chamber has a base pressure of $5 \times 10^{-10}$ Torr. Ultrapure Ar gas (99.9995%, Matheson Tri Gas) was first purified by a Matheson NanoChem Purifilter to achieve a specified impurity level of 1 ppb before sent into the sputtering chamber. Two types of substrates were used for Si nanowire synthesis: commercial Si (100) wafers with a 3000 Å thick thermal oxide layer for non-epitaxial growth and Si (111) substrates for epitaxial growth. All substrates were cleaned by sonication in acetone for 5 min followed by isopropanol for another 5 min, then rinsed with de-ionized water and blown dry with nitrogen. In addition, for epitaxial nanowire growth, the Si (111) substrates were treated with buffered HF for 20 s to remove the native oxide layer and rinsed with de-ionized water just before loaded into the load lock.
We used Au as the catalysts for Si nanowire growth. For Si wafers with thermal oxide layer, a Au (15 Å) / Si (8 Å) / Si (15 Å) trilayer was sputter deposited on the substrate as the catalysts at an Ar pressure of 5 mTorr. The deposition rate of Au is 0.5 Å/ s using a dc power supply and that of Si is 0.4 Å/ s using an rf power supply at 30 W. For clean Si (111) substrates, a 15 Å thick Au layer was used as catalysts. The substrate temperature was then increased to 600 °C. Si nanowires were grown for an hour by RF sputtering an undoped Si target (99.9999%) with a power of 75 W and Ar pressure of 5 mTorr. After the Si nanowire synthesis, field-emission SEM was used to characterize the nanowires.

![Fig.5.3 Set up of our UHV sputtering system](image)

### 5.3 Results and discussion

We first tried to grow Si nanowires on Si (100) wafers with a 3000 Å thick thermal oxide layer using a single 10–30 Å thick Au layer as catalyst. However, essentially no nanowires were observed. Instead, a polycrystalline layer of Si formed on
the substrate. This is likely due to that the arriving Si atoms formed a layer on top of Au and did not have enough time to diffuse into Au to form Au–Si liquid alloy at the substrate temperature of 600 °C, which is needed for Si nanowire growth via VLS mechanism. To promote the formation of Au–Si liquid alloy, we deposited a Au (15 Å) / Si (8 Å) / Si (15 Å) trilayer on thermally oxidized Si (100) substrate before raising the substrate temperature to 600 °C. The composition of the trilayer is near the eutectic point (~20% mole Si, 361 °C) of Au–Si alloy. As the substrate temperature exceeds 361 °C, the trilayer gradually forms Au–Si liquid nano-droplets due to the inter-diffusion of Si and Au in the trilayer to seed Si nanowire growth. After 1 hour growth, we observed Si nanowires on the surface of the substrate, as shown in Fig. 5.4. The nanowires are typically a few micrometers long with diameters of 200–300 nm. The shape of the nanowires is not cylindrical (inset of Fig. 5.4.a) as typically seen in VLS growth nanowires. It appears that during the Si deposition, in addition to the nanowire growth along the axial direction catalyzed by the Au–Si liquid alloy, there is also Si growth on the side of the nanowires. One possible reason for the side growth is that at the substrate temperature of 600 °C, some Si atoms arriving at the nanowire surface stick to the side of the nanowires.
Fig. 5.4 SEM images of silicon nanowires grown on the surface of a Si (100) substrate with a thermal oxide layer catalyzed by Au (15 Å) / Si(8 Å) / Si(15 Å) trilayer (inset: a single Si nanowire at higher magnification), (b) initial stage of the Si nanowire growth on cleaved side of the Si(100) substrate, which is believed to be (111) surface (inset: a few short nanowires with Au–Si catalysts at higher magnification), and (c) long Si nanowires grown on cleaved side of the Si(100) substrate.
More interesting nanowire growth was found at the side of the thermally oxidized Si (100) substrates, where the cleaved surface exposes fresh single-crystalline Si surface with various orientations. On some area at the side of the substrate, we observed Si nanowires grown out of the substrate, as shown in Fig. 5.4 (b) and (c). We believe that these nanowires were catalyzed by Au deposited on the side of the substrates. The short nanowires in Fig. 1(b) indicate initial stage of the nanowire growth with a clear Au–Si alloy sphere on top of each nanowire [inset of Fig. 5.4 (b)]. The nanowire growth out of the substrate surface suggests epitaxial growth of the Si nanowires, for which the substrate orientation is essential. We noticed that the areas with epitaxial Si nanowires on the cleaved sides have their surface at an estimated angle of 50°–60° with respect to the Si (100) surface, which is close to the 54.7° between (100) and (111) planes in a cubic lattice. Thus, it is likely that Si nanowires prefer epitaxial growth on Si (111) surface, which agrees with the consensus that semiconductor nanowires with cubic crystal structure favors growth along the (111) orientation. This assumption is supported by that essentially no nanowires are observed on other area on the cleaved sides with other crystal orientations. Fig. 5.4 (c) shows that although most of the nanowires are out of plane, they are not all perpendicular to the substrate. Instead, there are a few growth orientations with respect to the substrate normal. We will discuss this phenomenon next.

In order to control the epitaxial nanowire growth, we investigated the growth of Si nanowires on clean Si (111) wafers. A 15 Å Au film was deposited on buffered HF-etched Si (111) substrate before the substrate temperature was raised to 600 °C. After 1 hour sputtering, Si nanowires with diameters of 50–100 nm and length up to 8 µm were observed on the Si (111) surface, as shown in Fig. 5.5. The single Au layer works as
catalysts on clean Si (111) surface because Au absorbed Si out of the substrate during the heating of the substrate to form Au–Si liquid alloy; while there is no Si for Au to absorb if the substrate is silicon oxide as discussed above. It is clearly seen from the plan view in Fig. 5.5 (a) and (b) that most of the nanowires are along one of three orientations that are 120° way from each other, as guided by the inset in Fig. 5.5 (a). These three preferred growth orientations are determined by the cubic crystal geometry of the Si (111) substrate. In addition to the (111) direction normal to the substrate surface, there are three equivalent (111) orientations which are each 70° away from the substrate normal, as illustrated in Fig. 5.5 (c) and the inset in 5.5 (a). The nanowires grown perpendicular to the substrate surface are difficult to see from the plan view of the SEM images. This nanowire growth geometry has also been observed in GaAs nanowires grown on Si (111) substrates. As the substrate temperature was increased to the growth temperature of 600 °C, the Au film starts to absorb Si from the substrate at temperatures above the eutectic point of 361 °C and forms alloy nano-droplets, which create a “pit” in the Si substrate under each nanodroplet. During the initial stage of the nanowire growth, when the sputtered Si atoms supersaturate the nanodroplets and Si nanowires start to grow, the Au–Si alloy nanodroplets “see” all four equivalent Si (111) interfaces. The growth direction of the initial nanowires is random along one of the four directions, resulting in the observed nanowire growth geometry in Fig. 5.5.
Fig. 5.5 a) Plan-view SEM image of Si nanowires epitaxially grown on Si (111) surface. The nanowires grow along one of the four \( \langle 111 \rangle \) directions: [111], [11\( \bar{1} \)], [1\( \bar{1} \)1], and [\( \bar{1} \)11], as indicated by the inset. (b) A close-up view of the SEM image in (a). (c) Schematic of four \( \langle 111 \rangle \) orientations in a cubic lattice. (d) Tilt-view SEM image of a Si nanowire with growth direction perpendicular to the substrate surface. The diameter of the nanowire is 45 nm. The short irregular shaped Si nanowires are nonepitaxial Si nanowires. (e) Tilt-view SEM image of a Si nanowire with a diameter of 45 nm grown along one of the three off-normal \( \langle 111 \rangle \) orientations (inset: high magnification SEM image of the end of the nanowire).
Individual Si nanowires grown along surface normal and one of the three off-normal directions are shown in Fig. 5.5(d) and (e), respectively. These two nanowires are ~2 \( \mu \)m long and 45 nm in diameter. The Au–Si alloy catalysts are clearly seen on the top of each nanowire, as shown in the inset of Fig. 5.5(e). The Si nanowires in Fig. 5.5(d) and (e) have cylindrical shape with uniform diameter and smooth surface, much better than the non-epitaxial Si nanowires in Fig. 5.4. We also noticed that some nanowires in Fig. 5.5 (a) are not as uniform as those in Fig. 5.5(d) and Fig. 5.5 (e), indicating that Si growth on side of the nanowires still happens on some nanowires. One possible reason is that due to the growth geometry of magnetron sputtering and arriving angles of the Si atoms, nanowires grown along perpendicular direction to the substrate have much smaller chance to grow sideways compared to those with their axes at a large angle with respect to the surface normal of the substrate. In addition, there are also some short nanowires with irregular shape in Fig. 5.5(d) and (e). These nanowires are typically larger in diameter than the nanowire in the center of the figure and do not appear to be epitaxially grown on the substrate, similar to those grown on thermally oxidized Si substrates. It appears that nanowires with epitaxial relationship with the Si (111) substrate and small diameter preferably absorbs the sputtered Si atoms and grow faster than the nanowires with large diameter.

5.4 Conclusion

We have synthesized Si nanowires using ultrahigh vacuum sputtering. Si nanowires with diameters of 200–300 nm were obtained on thermally oxidized Si
substrate using Au (15 Å) / Si (8 Å) / Au (15 Å) trilayer as catalysts. Si nanowires with
diameter between 50 and 100 nm and length up to 8 µm were synthesized using epitaxial
growth on Si (111) substrates. Sputter provides an alternative fabrication route for Si
nanowire synthesis to more commonly used CVD and PLD techniques.
Chapter 6

Angular dependence of Photoluminescence of InP Nanowires

6.1 Introduction

6.1.1 Physical and electrical properties of InP

Indium phosphide (InP) is a direct-band gap III-V compound semiconductor crystal. InP is especially noted for its high operating speeds (40Gbits/sec or above for InP based High Electron Mobility Transistors), low noise, low voltage and high reliability. It is used in both photonic and electronic applications. Typical photonic device types include: lasers, photo-detectors, avalanche photo-diodes, optical modulators and amplifiers, waveguide-based devices, quantum photonic devices, and both optoelectronic and photonic integrated circuits as well as new devices for optical communications, switching, networking, signal processing and leading edge material for solar cells [66, 96-98].
InP nanowires usually have the same zinc-blende (ZB) crystal structure as bulk material. In zinc-blende InP nanowires, the space lattice is face centered cubic (FCC) with a basis of two atoms, which can also be viewed as two FCC lattices that are separated by 1/4 of the body diagonal of the unit cube. One lattice is occupied by In atoms, the other by P atoms. Each atom has 4 nearest neighbors of the opposite kind and is bound to these 4 atoms which are arranged at the corners of the surrounding tetrahedron. The bonding is typically covalent. The crystal structure of InP crystal is shown above in Fig. 6.1. Other important physical properties of InP at room temperature are shown in Table 6.1.
Table 6.1 Physical properties of InP bulk at room temperature

<table>
<thead>
<tr>
<th>Properties</th>
<th>Parameter Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
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</tr>
<tr>
<td>Lattice constant</td>
<td>5.87 Å</td>
</tr>
<tr>
<td>Density</td>
<td>4.81 g/cm³</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>145.792</td>
</tr>
<tr>
<td>Coefficient of thermal expansion</td>
<td>$4.6 \times 10^{-6} \text{ K}^{-1}$</td>
</tr>
<tr>
<td>Specific heat</td>
<td>0.31 J/g·K</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.68 W/cm²·°C</td>
</tr>
<tr>
<td>Dielectric constant</td>
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</tr>
<tr>
<td>Band gap</td>
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</tr>
<tr>
<td>Threshold field</td>
<td>50 kV/cm</td>
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<tr>
<td>Peak drift velocity</td>
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<tr>
<td>Electron mobility (Room Temperature)</td>
<td>5400 cm²/V·s</td>
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<tr>
<td>Hole mobility (Room Temperature)</td>
<td>200 cm²/V·s</td>
</tr>
<tr>
<td>Melting point</td>
<td>1060°C</td>
</tr>
</tbody>
</table>

Table 6.1 Physical properties of InP bulk at room temperature

6.1.2 Band structure of InP Bulk

The band structure of bulk InP is shown in Fig. 6.2. The electrons in the conduction band have s-type wave function which has total angular momentum $J = \frac{1}{2}$ (orbital angular momentum $l = 0$ and spin momentum $s = \frac{1}{2}$) resulting a two-fold degeneracy at $k = 0$. In the valence band, the electronic states become more complicated
due to the spin-orbit interaction. The spin-orbit interaction splits the valence band into heavy-hole \((hh)\) band, light-hole \((lh)\) band and split-off band. For each band, there are 2 folds degeneracy if spin is included. The heavy holes and light holes in the valence band have p-type wave functions with total angular momentum \(3/2\) \((l = 1\) and \(s = 1/2\)). The heavy holes \((hh)\) have spin angular momentum \(3/2\) \((m_J = \pm 3/2)\) and light holes \((lh)\) have \(m_J = \pm 1/2.\) While the split-off band has a total angular momentum \(J = 1/2\) and spin angular momentum \(m_J = \pm 1/2.\)

When an electron in the conduction band recombines with a hole in the valence band, total momentum has to be conserved, which requires that the total angular momentum has to be equal to the angular momentum of a photon \((\pm 1)\). It follows that there are only four possible recombination possibilities, in term of spin conservation: \(|\frac{3}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, -\frac{1}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle, |\frac{1}{2}, \frac{1}{2}\rangle\). Also, due to the large spin-orbit coupling energy (for example \(E_{SO} \sim 111\) meV for InP), the recombination processes between conduction electrons and holes in the split-off band are often ignored because they are not thermally populated \([99]\).
6.1.3 Size effect on band structures of InP nanowires

It’s well known that the band gap of semiconductor nanowires increases as the wire diameter decreases. There are numerous theoretical works on this subject. However, a simple Effective Mass Model (EMM) could be used to explain the size dependence of band gap of semiconductor materials to the first order [100].
In 2002, Lieber’s group applied the EMM model in 2-dimensional cylindrical potential for electrons and holes [12]. In this model, particle-in-a-cylinder wave functions are used for both electrons and holes:

\[ \psi(r_e, r_h, z_e, z_h) = N J_0(\alpha_{01} r_e R) \sin(\pi z_e L / L) \]  

(6.1)

where \( J_0(\alpha_{01} r_e / R) \) is the zeroth-order Bessel function, \( \alpha_{01} \) is the first zero value of the zeroth-order Bessel function, \( L \) is the length of the cylinder, and \( N \) is the normalization constant. The calculated energy shift \( \Delta E \), relative to the bulk band gap as a function of the nanowire radius \( R \), is given by

\[ E = \frac{\hbar^2}{2m^*} \left( \frac{\alpha_{01}}{R} \right)^2 + \left( \frac{\pi}{L} \right)^2 \left( \psi(x_e) \psi(x_h) \left| \frac{e^2}{\epsilon |x_e - x_h|} \right| \psi(x_h) \psi(x_e) \right) \]  

(6.2)

where \( m^* \) is the reduced effective exciton mass \( (m_e m_h )/(m_e + m_h) \), \( \hbar \) is Planck’s constant, \( e \) the electron charge, and \( \epsilon \) the dielectric constant of InP. The first term represents the size-dependent kinetic energy confinement imposed by the walls of the nanowire cylinder. The second term is the attractive Coulomb interaction between electron and hole to first order in perturbation theory. The Coulomb interaction was numerically evaluated using the Green’s function expansion in terms of Bessel functions:

\[ \frac{1}{|x_e - x_h|} = \sum_{m = -\infty}^{\infty} \int_{0}^{\infty} e^{i m (\varphi_e - \varphi_h)} J_m(kr_e) J_m(kr_h) e^{-k|z_e - z_h|} dk \]  

(6.3)

where \( J_m(kr_e) \) is the \( m \)-th order Bessel function.

Lieber’s experiment data [12] are well fit by the EMM at room temperature and 7 K as shown in Fig. 6.3, which used the reduced effective mass \( m^* \) as the primary fitting parameter. The good fit of the experimental data suggests that this model captures the essential physics of the system. The reduced effective mass at room temperature
determined from the fit, $0.052 \, m_0$ ($m_0$, the free electron mass), is in reasonable agreement with the literature value of $0.065 \, m_0$ (calculated using $m_e = 0.078$ and the geometric mean of the anisotropic hole masses, $m_h = 0.40$) for bulk InP [101]. The value of the reduced mass determined from the 7 K data, $0.082 \, m_0$, is larger than the room temperature value but consistent with the observation that the effective carrier masses in InP increase with decreasing temperature within the accuracy of the known data.
Fig. 6.3 a) PL spectra taken at room temperature from single InP NWs with nominal diameters of 50, 20, 15, and 10 nm. (b) Single NW PL spectra at 7 K. (c) Emission energy maxima at RT versus NW diameter. (d) Emission energy maximum at 7 K. The experimental data in (c) and (d) were fit using the EMM (solid line) [12]

6.2 Synthesis of InP nanowire

Substrate for nanowire growth is made by functionalizing the surface of a silicon substrate (Silicon with 500 nm thermal oxide) for 15 minutes sonication in Acetone, 15 minutes sonication in Methanol, treatment of 1 hour UV-Ozone and then 15 minutes with
a solution of 0.1% poly-L-lysine (Ted Pella). Gold nano-colloid solution (0.01% concentration, BBI International) with size of 50 nm is dispersed onto substrate. After 15 minutes, the substrate is quickly (less than 10 seconds) rinsed with DI water and blown dry with nitrogen, while gold nano colloid are left and attached to the substrate. InP target is made from 2g InP polycrystalline powder (99.999%, Alfa Aesar) which is ground for 2 hours and pressed for 12 hours. Target doping can be realized by mix In$_2$Se$_3$ powder (99.99%, Alfa Aesar) with InP powder. For example, 0.1% Se doped Target can be made of 1.06 mg In$_2$Se$_3$ and 1g InP.

PLD system comprised of a KrF excimer laser and a quartz tube furnace is schematically shown in Fig.6.4. A pressed target is positioned to the right at the upstream end of a three-zone furnace. The Au nano-colloid functionalized substrate is loaded in the quartz tube between the center and the downstream end of the furnace. The quartz tube is evacuated by a mechanical pump to base pressure below 10 mTorr before the furnace starts to heat up. The temperature at the center of the furnace, $T_{\text{center}}$ is controlled at
850°C. The location of the substrate is typically 9 inches from the center of the furnace on the downstream side, giving a growth temperature of the substrate $T_{\text{sub}}$, between 450 and 550°C, which could be controlled by a left zone heater. Once the growth temperature is reached, an argon flow of 50 – 100 Standard Cubic Centimeters per Minute (sccm) is sent in with the pressure in the quartz tube controlled at 50 - 100 Torr. Then, a 2 Hz pulsed laser beam with a wavelength of 248 nm and duration of 10 ns is focused onto a 2.4 × 3.9 mm² spot on the InP target to start the ablation which produces In and P vapors. The laser energy density is maintained at 1 - 2 J/cm² per pulse. A typically growth duration is 10 – 30 minutes. Fig 6.5 shows an SEM image of the InP nanowires. Fig 6.6 shows high resolution TEM (HRTEM) images of a single wire. The core structure is single crystal, and outer shell is an oxide layer.
Fig. 6.5 InP nanowires grown via PLD system with Growth Temperature $T_{\text{sub}} = 500^\circ$C, growth time $t = 30$ minutes, constant Ar flow rate 50 sccm, base pressure $P = 100$ Torr, laser density $1.5$ J/cm$^2$, laser frequency 2Hz.

There are three major factors affecting the optimum growth conditions: Temperature, laser energy and target surface condition. Temperature is the most dominant factor. $470 – 520$ °C is the temperature window at which we have obtained best samples. If the growth temperature is below $470^\circ$C, nanowires deviate from cylindrical wire geometry and become zigzag in shape. If the temperature is above $520$ °C, no wires are grown on the substrate. The ratio of P and In vapor pressures is critical for the formation of nanowires. In MOCVD system, the group V vapor rich environment is required for III-V semiconductor growth. In PLD system, it is tricky to control the III-V vapor ratio. During the initial stage of the laser ablation on a new InP target, the amount
of P vapor generated is more than that of the In vapor because P is more volatile than In. The extra loss of P relative to In from the target leaves more In than P on the surface of the target, which leads to less P and more In vapor generated by the ablation with time. Therefore, a relatively fresh target surface and moderate laser energy (1 - 2 J/cm² per pulse) benefits the growth.

Fig.6.6. High resolution TEM image of single crystal InP nanowire. The core structure is single crystal along (111) direction and outer shell is oxide layer. Bottom right is Fourier-transformation of core structure.
6.3 Angular dependence of photoluminescence (PL) of random ensemble of InP nanowires

6.3.1 Motivation

Due to the anisotropy of nanowire geometry, the intensity of photoluminescence of nanowire has strong dependence on the angle between the polarization of excitation beam and the nanowire axis. As shown Fig. 6.7, the PL intensity for the incoming beam parallel to the nanowire axis is orders of magnitude higher than the perpendicular alignment [102]. For this single nanowire case, the polarization anisotropy could be as high as 96%. This property of nanowire is important for fundamental studies of polarization-sensitive electronic states and potential applications in polarization-sensitive photodetectors. Being able to control the anisotropy has been the interest of our work.
Fig. 6.7 Polarized excitation and emission spectra of NWs. (A) Excitation spectra of a 15-nm-diameter InP NW. These spectra were recorded with the polarization of the exciting laser aligned parallel (solid line) and perpendicular (dashed line) to the wire (B) Emission spectra of the same wire as in (A). The polarization ratio of the parallel (solid line) to perpendicular (dashed line) emission is 0.92. Inset, plot of the polarization ratio as a function of energy. (C) Dielectric contrast model of polarization anisotropy. The nanowire is treated as an infinite dielectric cylinder in a vacuum while the laser polarizations are considered as electrostatic fields oriented as depicted. Field intensities ($|E|^2$) calculated from Maxwell’s equations clearly show that the field is strongly attenuated inside the nanowire for the perpendicular polarization, $E_\perp$, whereas the field inside the nanowire is unaffected for the parallel polarization, $E_\parallel$ [102].

This large polarization response can be accounted for in terms of the large dielectric contrast between the nanowire and its surrounding environment. This effect can be quantitatively modeled by treating the nanowire as an infinite dielectric cylinder in a
vacuum, when the incident field is polarized parallel to the cylinder, the electric field inside the cylinder is not reduced.

\[ E_{i\parallel} = E_{e\parallel} \]  \hspace{1cm} (6.4)

But when polarized perpendicular to the cylinder, the electric field amplitude is attenuated because the wavelength of the exciting light is much greater than the wire diameter [103].

\[ E_{i\perp} = \frac{2\varepsilon_0}{\varepsilon + \varepsilon_0} E_{e\perp} \]  \hspace{1cm} (6.5)

where \( E_i \) is the electric field inside the cylinder, \( E_e \) the excitation field, and \( \varepsilon (\varepsilon_0) \) is the dielectric constant of the cylinder (vacuum). With dielectric constant for bulk InP of 12.4, a theoretical polarization ratio can be calculated as,

\[ \rho = \frac{(I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp}) = (E_{\parallel}^2 - E_{\perp}^2)/(E_{\parallel}^2 + E_{\perp}^2) = 0.96,} \]  \hspace{1cm} (6.6)

which is in excellent agreement with the maximum values determined in experiment of Lieber’s paper [102].

Fig 6.8 Schematic of electrical field in a cylindrical nanowire
Pervious works are all based on nanowires in vacuum environment as shown above, most of which are trying to obtain maximum polarization anisotropy. However, isotropy of polarization is needed in some cases. For example, circularly polarized light is required for spin polarized absorption and emission in III-V semiconductor nanowires [104, 105]. Circularly polarized light becomes linear polarized when entering from vacuum environment into InP nanowire. Hence, it is essential to change the dielectric constant of environment $\epsilon_o$ in order to minimize the polarization anisotropy for spin studies in nanowires [106].

6.3.2 Tuning PL anisotropy of nanowires via oxide coating

6.3.2.1 Experiment Setup

Other than measuring PL spectra on each individual nanowire, ensemble of nanowire samples is measured in our work. As shown in Fig. 6.9, the as-grown nanowire sample is loaded in a magneto-optical cryostat (Oxford instrument). The sample is then cooled down to 5K and excited by a 690 nm wavelength laser beam from a Mode-locked Ti:Sapphire laser. The excitation light is reflected from a dichroic mirror and focused on an objective to a $\sim 100 \, \mu m$ diameter spot on the nanowire sample. The typical excitation power is $\sim 5 \, mW$. The resulting PL is collected by the same objective, passes through a long-pass through filter to remove the excitation light, focuses on an entrance slit of a spectrometer with 300 mm focus length. The spectra are collected by a liquid-nitrogen cooled charge-coupled device (CCD) system. The linear polarization of NWs is analyzed.
by two linear polarizers in the pump and collection path, with a half-wave plate in the pump path to change the linear polarization of pump beam.

Fig. 6.9 (Left) Magneto-optical Cryostat; (Right) Mode-locked Ti:Sapphire laser

6.3.2.2 Experimental results

Fig 6.10 shows a typical SEM image and a PL spectrum of as-grown InP nanowires. The InP nanowire sample is synthesized by PLD as described in section 6.1.

The nanowires are cylindrical shaped and have smooth surfaces. The diameter ranges from 60 to 80 nm and length ranges from 15 to 40 µm. All those wires have random orientations on SiO$_2$ substrate. In Fig.6.11, the shaded area is mainly the NW luminescence. The peak is centered at 849 nm. The broad feature of the peak is largely due to the inhomogeneity of nanowire diameters. The spectrum is asymmetric and has a
trail at lower energy end, which is due to surface defects and nucleation in bulk/ film form during growth. And there is a satellite peak around 890 nm, which may be contributed from polycrystalline compounds formed on wire surface. As a comparison, the band gap of bulk InP at 5K is 1.42 eV which corresponds to 873 nm. By comparing band gaps between bulk InP and InP nanowires, there is a blue shift caused by quantum confinement. The blue shift confirms Effective Mass Method and results from Lieber’s group [12] as mentioned in Chapter 6.1.3. The PL signal contains emissions from bottom of the conduction band to heavy holes, emissions from bottom of the conduction band to light holes and other emissions from defect states below conduction band. Due to the limitation of resolution and small energy split (a few meV) between heavy holes and light holes in NWs, it is hard to distinguish the emissions between heavy holes and light holes from the spectrum.

![SEM image of InP nanowires by PLD](image_url)

Fig. 6.10 SEM image of InP nanowires by PLD
6.3.2.3 Polarization anisotropy of ensemble of InP Nanowires

Most of the PL studies on nanowires are based on single nanowire emission. Wang et al [102] have shown large PL anisotropy on single InP nanowire. PL spectra were taken from a number of individual nanowires as a function of excitation or emission polarization. In both cases, the ratio of parallel to perpendicular emission is greater than an order of magnitude. The order-of-magnitude polarization anisotropy is exhibited over most of the energy range of the PL peak and for excitation with both 488- and 514-nm laser wavelengths. On average, the measured excitation and emission polarization ratios, \( \rho = (I_\parallel - I_\perp)/(I_\parallel + I_\perp) = (E_\parallel^2 - E_\perp^2)/(E_\parallel^2 + E_\perp^2) \) of the intensities parallel \((I_\parallel)\) and perpendicular \((I_\perp)\) to the wire axis are 0.91 ± 0.07. Many nanowires exhibited a polarization ratio of 0.96. The polarization ratio was independent of nanowire diameter between 10 and 50 nm, but radial quantum confinement effects were observed for
diameters \leq 20 \text{ nm}. This large polarization response can be accounted for in terms of the large dielectric contrast between the nanowire and its surroundings environment which was mentioned in Chapter 6.1.3.

Fig. 6.12 Schematic of angular dependence PL measurement on random ensemble of nanowires

Our study on PL based on random ensemble of InP nanowires as shown in Fig. 6.12. The nanowires have random orientations on the substrate and each single nanowire has its own polarization anisotropy. When an excitation beam passes through linear polarizer and hits the sample, those wires oriented parallel to the direction of the beam will absorb and emit more light than perpendicular ones. And as an ensemble, there is polarization contribution from different orientations so we should still get a polarization response as shown in Fig. 6.12. In our experiment setup, we are not going to use the angle between the excitation polarization and NW axis due to the randomness of the NW. Therefore, we have linear polarizers in the excitation and detection path. A half
waveplate is put in the pump path to change the polarization of excitation beam, as a result, we change the angle $\theta$ between excitation and detection polarizations and detect the PL intensity dependence with the angle.

![Graph showing angular dependent PL spectrum of ensemble InP nanowires at temperature of 5K](image)

Fig 6.13 Angular dependent PL spectrum of ensemble InP nanowires at temperature of 5K

As shown in Fig 6.13, as we change the polarization of the incoming beam, the intensity of the PL changes. Between PL intensities of the parallel and perpendicular alignments of the incident beam and detection polarizations, the parallel case is about twice higher intensity than perpendicular case. The satellite peak at 890 nm, which is not from NWs, has much less polarization dependence. The PL intensity is directly related to the polarization angle difference between the incoming beam and the detection polarizer.
A more careful angular dependence measurement of PL spectra has been taken. By rotating the half wave plate with small angle steps, we recorded the PL intensity at each angle, normalized it with the highest intensity obtained and plotted it as a function of angle. We found that the PL intensity oscillates with the angle at a period of 180°, reaches maximum and minimum every 90 degree.

Fig. 6.14 Schematic of emission incidents electric fields and nanowire orientation

We developed a model to explore the relation between the intensity and θ for our ensemble nanowire sample. This model is based on our experimental scheme for randomly oriented ensemble nanowires and theoretical paper published by H.E.Ruda [107]. As shown in Fig. 6.14, γ is the angle between nanowire axis and the polarization
direction of the detection polarizer, while \( \theta \) is the angle between polarization directions of the incoming and detection polarizers. The dielectric constants of nanowires and medium are \( \varepsilon \) and \( \varepsilon_0 \), respectively. The final PL intensity detected by CCD is composed to two parts: absorption and emission. For each part, the parallel component of polarization direction stays the same but the perpendicular component attenuates due to dielectric constant contrast. Hence the final light intensity detected by CCD can be express as:

\[
\int_0^\pi [E_0 \cos(\theta - \gamma)]^2 \left[ (\cos \gamma)^2 + \frac{6\varepsilon_0^2}{(\varepsilon_0 + \varepsilon_1)^2 + 2\varepsilon_0^2} (\sin \gamma)^2 \right] d\gamma \\
+ [E_0 \frac{2\varepsilon_0}{\varepsilon_0 + \varepsilon_1} \sin(\theta - \gamma)]^2 \left[ (\cos \gamma)^2 + \frac{6\varepsilon_0^2}{(\varepsilon_0 + \varepsilon_1)^2 + 2\varepsilon_0^2} (\sin \gamma)^2 \right] d\gamma
\]

\( = \int_0^\pi [E_0 \cos(\theta - \gamma)]^2 (\cos \gamma)^2 d\gamma \\
+ \int_0^\pi [E_0 \frac{2\varepsilon_0}{\varepsilon_0 + \varepsilon_1} \sin(\theta - \gamma)]^2 (\sin \gamma)^2 d\gamma
\]

\( + \int_0^\pi ([E_0 \frac{2\varepsilon_0}{\varepsilon_0 + \varepsilon_1} \sin(\theta - \gamma)])^2 (\cos \gamma)^2 d\gamma \\
+ \int_0^\pi ([E_0 \frac{2\varepsilon_0}{\varepsilon_0 + \varepsilon_1} \sin(\theta - \gamma)])^2 (\sin \gamma)^2 d\gamma
\]

\( (6.7) \)

And the normalized PL intensity can be expressed as

\[
\left| \frac{(10\varepsilon_0^2 + 4\varepsilon_0\varepsilon_1 + 2\varepsilon_1^2)(9\varepsilon_0^2 + 2\varepsilon_0\varepsilon_1 + \varepsilon_1^2) + (\varepsilon_0 - \varepsilon_1)^2 (3\varepsilon_0 + \varepsilon_1)^2 \cos(2(\theta - 90) * 2 * \pi * 360)}{8(\varepsilon_0 + \varepsilon_1)^2 (3\varepsilon_0^2 + 2\varepsilon_0\varepsilon_1 + \varepsilon_1^2)} \right| \\
\times \varepsilon_0^2 \times \pi
\]

\( (6.8) \)

Based on Eqn. 6.8, we plot the relationship of the PL intensity versus polarization angle between excitation and detection, which is a function of the dielectric constants of
the NWs and their environment. After plugging in the dielectric constants of InP ($\varepsilon = 9.6$) and air ($\varepsilon_0 = 1$), an angular dependence of polarization is plotted as blue curve in Fig.6.15. The experimental data is obtained and marked as red dotted link, which correlates well with our model.

![Fig. 6.15 PL intensity versus angle between excitation and emission lights](image)

Fig. 6.15 PL intensity versus angle between excitation and emission lights

In order to tune the polarization of anisotropy, one of the approaches is to change the environment surrounding the nanowires. Ta$_2$O$_5$ is a well known high-k material with dielectric constant of ~4.4 at optical frequencies. Using ultra high vacuum sputtering, a 500nm ~ 600 nm thick Ta$_2$O$_5$ is uniformly coated onto the same InP nanowire sample,
which is as shown in Fig. 6.16. PL spectra are taken at temperature of 5K as shown in Fig. 6.17.

The PL of oxide coated sample peaks at 867 nm instead of 849 nm for bare nanowires, which most likely due to the creation of some shallow defect states below conduction band during the oxide coating. As we change the polarization angle between emission and detection beam, the PL intensity has very different response to the angle from the bare wires. The polarization anisotropy is greatly attenuated as shown in Fig. 6.18 where the intensities of the parallel and perpendicular cases are almost identical.

Fig. 6.16 SEM image of ensemble InP nanowires with Ta$_2$O$_5$ coating
Fig. 6.17 PL spectrum of ensemble InP nanowires with Ta$_2$O$_5$ coating at 5K

Fig. 6.18 Angular dependent PL spectrum of Oxide coated InP nanowires at T = 5K
Same as for bare nanowires, we made a detailed measurement of angular dependence PL on oxide coated nanowires. As shown in Fig. 6.19, the intensity still oscillates but with much less change in amplitude with respect to the angle. With oxide coating, the polarization anisotropy is significantly reduced, and the anisotropy is about only 2.6%. For oxide coated InP nanowires, the dielectric constant of media is now 4.4 ($\text{Ta}_2\text{O}_5$) instead of 1 (Air). Based on model mentioned above, the PL intensity with respect to angle is plotted in Fig. 6.19. Again this line does not have any free parameters. The result agrees with our measurement and is consistent with bare wires results.

![Fig. 6.19 PL intensity versus angle between excitation and emission lights with oxide coating of ensemble InP nanowires](image)

Fig. 6.19 PL intensity versus angle between excitation and emission lights with oxide coating of ensemble InP nanowires
6.4 Conclusion

We have synthesized InP nanowires using PLD. PL spectra are carefully studied on ensemble InP nanowires. Blue shift in energy gap is observed which confirms other experimental results on single free standing nanowire. Angular dependence of PL spectra are studied which matches well with the calculations using our model on ensemble nanowires. Tuning PL anisotropy of InP nanowires is realized by coating nanowires with Ta$_2$O$_5$. By picking environmental media whose dielectric constant is closed to the nanowires make optical spin injection into III-V nanowires possible. This may lead to more thorough spintronics studies of semiconductor nanowires.
Summary

Recently, 1-D structures such as nanowires have become the focus of intensive research of owing to their unique applications to mesoscopic physics and fabrication of nano scale devices. For nanowire synthesis, challenges such as size, shape, position, stoichiometry and defect control still exist. Due to the dimensionality and possible quantum confinement effects of nanowires, there are also challenges in characterization and device fabrication. In this dissertation, a systematic study of semiconductor nanowire synthesis has been conducted with fabrication methods of PLD, ultra high vacuum sputtering and CVD. Electric and optical characterizations have been studied.

In chapter 4, we have systematically studied the synthesis conditions for GaAs nanowires using PLD with various arsenic overpressures. Arsenic over-pressure with As$_2$ molecules is introduced into the system by thermal decomposition of polycrystalline GaAs. Long single-crystal GaAs nanowires with uniform diameter, small diameter distribution and thin surface oxide layer were obtained. A preliminary electrical characterization on an individual GaAs nanowire gives a linear I–V curve with a reasonable resistance.

In chapter 5, we have synthesized Si nanowires using ultrahigh vacuum sputtering. Si nanowires with diameters of 200–300 nm were obtained on thermally oxidized Si
substrate using Au (15 Å) / Si (8 Å) / Au (15 Å) trilayer as catalysts. Si nanowires with diameter between 50 and 100 nm and length up to 8 µm were synthesized using epitaxial growth on Si (111) substrates. Sputter provides an alternative fabrication route for Si nanowire synthesis to more commonly used CVD and PLD techniques.

In chapter 6, InP nanowires have been synthesized via PLD System. PL spectra are carefully studied on ensemble InP nanowires other than single free standing nanowire. Blue shift in energy gap is observed which confirms other experimental results on single free standing nanowire. Angular dependence of PL spectra are studied which matches well with our theoretical prediction on ensemble nanowires. Tuning PL anisotropy of InP nanowires is realized by coating nanowires with Ta₂O₅. By picking environmental media whose dielectric constant is closed to nanowire, optical spin injection into III-V nanowires is possible. This will lead to more thorough spintronics studies of semiconductor nanowires.
Bibliography


