

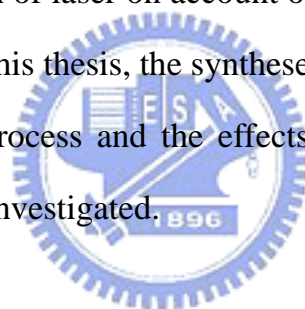
Chapter 1 Introduction

1.0 Preface

“Nano” the word is results in the well known speech by Dr. Richard P. Feynman gave on Dec. 29th 1959 at the annual meeting of the American Physical Society at the California Institute of Technology (Caltech)¹. The unique and fascinating properties of nanostructured materials have triggered tremendous motivation among scientists to explore the possibilities of using them in industrial applications especially in the electronic and optical properties of nanostructured materials have been of interest for their potential applications in the fabrication of microelectronic and electroptical devices.²⁻⁵ There are many of advantages in reducing the size of microelectronics: higher density of integration, faster response, lower cost, and less power consumption. With the development of microelectronics and electroptical devices, the techniques for the fabrication of nanomaterials have been extensively study. Worldwide attention is focused on nanostructured materials of different shapes, as films, wires, and dots, for their different geometry of the nanoscale materials with many peculiar physical phenomena include size dependent excitation, ballistic conductance, Coulomb blockade, single electron tunneling and metal-insulator transition. These studies mainly focused on zero-dimensional (0D) quantum dots and two-dimensional (2D) quantum well structures, while study of one-dimensional (1D) nanowires could have distinctive opportunities in understanding fundamental concepts and can exhibit unusual physical properties, such as field emission,⁶⁻⁷ electrical conductivity,⁸⁻¹² biological,¹³

magnetism,¹⁴ mechanical properties¹⁵⁻¹⁶ and visible photoluminescence¹⁷⁻¹⁸ due to quantum confinement effect,¹⁹ which differ from the bulk materials. There are many nanoscale devices, such as quantum dot lasers,²⁰⁻²¹ single electron transistor (SET),²² logic and memory units²³, light-emitting diode (LEDs),²⁴ and field emission display devices²⁵⁻²⁸ have been fabricated by numerous research group around the world.

Nanostructured materials represent an intellectually challenging and rapidly expanding area of research. These individual nanolasers could serve as miniaturized light sources for microanalysis, information storage, and optical computing. ZnO nanowires are considered as one of the most promising materials for the application of laser on account of its wide bandgap and higher exciton binding energy. In this thesis, the syntheses of ZnO nanowires by a new vapor-liquid-solid (VLS) process and the effects on the optical properties of ZnO nanowires have been investigated.



1.1 Motivation

The metal oxide materials, especially the transition metal oxides (B series in the periodic elements table) have many attractive properties. The wide band gap materials²⁹, such as ZnO, Ga₂O₃, GaN, In₂O₃, SnO₂, etc. which also have at least one direct band gap that can have well optical emission properties. The good optical emission ability for these materials studies are presents recently which many researchers attend more eyes in more potential for the nano laser applications.

The next generation display devices, field emission devices (FED)³⁰ in these years also focus on the new materials development. Metal oxides

nanowires have attractive properties as sources for field emitters³¹⁻³³, such as high aspect ratio, small radius of curvature, high mechanical strength and chemical stability. There have been many efforts to apply metal oxide nanowires to FEDs. But to achieve the objects of the demand of the FEDs, there are some problems can be solved. One is the higher turn-on electric field³⁴⁻³⁸, in general, the metal oxide such as ZnO NWs always have higher turn-on electric field which limits the application in the low voltage supply markets in the future. Then, the current density must be attending to enough level to emission the panel. Furthermore, the manufacture process needs to be easily integrated into the semiconductor industry that will help the nanowires type FEDs make to be commercialize in last decade³⁹⁻⁴⁰.

To improving these issues, the ZnO NWs is selected to be study the optical emission and the characteristics of field emission. Through a series of different synthesized process controlled methods the ZnO NWs is getting to suitable for field emission application results in the substantial turn-on electric field, more stable current density and lower series resistance. On the same time, the ZnO NWs also realize the triode which using the side gate controlled field emission devices. These study will speedy the ZnO NWs to apply to the FEDs in the future.

1.2 Material Properties

Nanostructures can be defined as systems in which at least one dimension is smaller than 100 nm; that is reducing 1, 2, or 3 dimensions (D) of a bulk material to the nanoscale produces 2D films, 1D nanowires, or 0D nanoclusters, respectively. In the past few years, 1D nanostructured materials, such as

nanowires,⁴¹⁻⁴³ nanorods,⁴⁴ nanotubes,⁴⁵ nanobelts⁴⁶⁻⁴⁷ and nanocables,⁴⁸⁻⁵¹ have draw much attention in basic scientific research and technology applications. Nanowires are anisotropic nanoparticles with high aspect ratios (length/diameter). In general, they have diameters of 1-100 nm and length of several micrometers. Many singular characteristics have been reported including fundamentals of mesoscopic phenomenon⁵² and the potential in the buildup of functional electronic, superior mechanic toughness, higher luminescence efficiency and lowered laser threshold and molecular computing to scanning probe microscopy tips. In addition, the nanowires can provide a material system to experimentally test fundamental quantum mechanical concepts.

1.2.1 Optical Properties



Due to the quantum confinement effect, the nanowires exhibit distinct optical properties⁵³⁻⁵⁴ when their size is below certain critical dimension; the blue shift of absorption edge of nanowires from the bulk materials, sharp discrete absorbance feature and relatively strong photoluminescence were observed.⁵⁵ The quantum size confinement effect is a basic characteristic of all low dimensional materials. The electrical and optical properties of nanowires are strongly size dependent. It is widely accepted that the quantum confinement of electrons by the various potential well of nanostructure control the electrical, optical, magnetic, and thermoelectric properties of the solid material. According to the solid state physics,⁵⁶ the dynamics of the electrons in crystals can be described by effective-mass approximation as

$$\left[-\frac{\hbar^2}{2m^*} \nabla^2 + V(\vec{r}) \right] \psi_{\vec{k}}(\vec{r}) = E(\vec{k}) \psi_{\vec{k}}(\vec{r}) \quad (1.1)$$

Where, m^* is the effective mass; \hbar is the Planck's constant divided 2π ; $\vec{r} = (x, y, z)$ is the electron position vector; $V(\vec{r})$ is the confinement potential; $\psi_{\vec{k}}(\vec{r})$ is the wave function (or eigenfunction); and $E(\vec{k})$ is the electron energy (or eigenstate). The eigenstates, eigenfunctions and density of state (DOS) for various quantum systems are as follows,

For bulk material,

$$E(\vec{k}) = E(k_x, k_y, k_z) = \frac{\hbar^2}{2m^*} (k_x^2 + k_y^2 + k_z^2) \quad (1.2)$$

$$\psi_{\vec{k}} = \frac{1}{\sqrt{V}} \exp[-i(k_x x + k_y y + k_z z)] \quad (1.3)$$

$$D(E) = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} E^{1/2} \quad (1.4)$$

For quantum well,

$$E(\vec{k}) = E_n(k_x, k_y) = \frac{\hbar^2}{2m^*} \left(k_x^2 + k_y^2 + \left(\frac{n\pi}{L_z} \right)^2 \right) \quad (1.5)$$

$$\psi_{\vec{k}} = \frac{1}{\sqrt{A}} \varphi_n(z) \exp[-i(k_x x + k_y y)] \quad (1.6)$$

$$\text{where } \varphi_n(z) = \sqrt{\frac{2}{L_z}} \sin \left[n\pi \left(\frac{z}{L_z} + \frac{1}{2} \right) \right] \quad (1.7)$$

$$D(E) = \frac{m^*}{\pi \hbar^2 L_z} \sum_n H(E - E_n) \quad (1.8)$$

For quantum wire,

$$E(\vec{k}) = E_{m,n}(k_x) = \frac{\hbar^2}{2m^*} \left(k_x^2 + \left(\frac{m\pi}{L_y} \right)^2 + \left(\frac{n\pi}{L_z} \right)^2 \right) \quad (1.9)$$

$$\psi_{\vec{k}} = \frac{1}{\sqrt{L}} \varphi_m(y) \varphi_n(z) \exp[-ik_x x] \quad (1.10)$$

$$D(E) = \frac{N_{WR}}{\pi} \frac{\sqrt{2m^*}}{\hbar} \sum_{m,n} \frac{1}{\sqrt{E - E_{m,n}}} \quad (1.11)$$

For quantum dot,

$$E(\vec{k}) = E_{l,m,n} = \frac{\hbar^2}{2m^*} \left(\left(\frac{l\pi}{L_x} \right)^2 + \left(\frac{m\pi}{L_y} \right)^2 + \left(\frac{n\pi}{L_z} \right)^2 \right) \quad (1.12)$$

$$\psi_{\vec{k}} = \frac{1}{\sqrt{L}} \varphi_l(x) \varphi_m(y) \varphi_n(z) \quad (1.13)$$

$$D(E) = 2N_D \sum_{l,m,n} \delta(E - E_{l,m,n}) \quad (1.14)$$

In Eq.(1.3), $V = L^3$ is the crystal volume. In Eq.(1.6), $A = L^2$ is the area of the quantum well, L_z is the well width, and the $H(x)$ is the Heaviside step function ($H(x)=1$ for $x \geq 0$ and $H(x)=0$ for $x < 0$). In Eq.(1.10), L is the length of the quantum wire, L_y is the y-direction length of the wire cross-section, and in Eq. (1.11), N_{WR} is the density of quantum wires. In Eq. (1.14), N_D is the volume density of quantum dots. Fig 1.2 shows the nanostructure and their DOS.

1.2.2 Field Emission Properties

It is well known that nanotubes⁵⁷⁻⁶¹ and nanowires⁶² with sharp tips are suitable materials for cold cathode field emission device application. Field emission characteristics of these 1D materials have been investigated using current-voltage measurements and the Fowler-Nordheim (FN) equation recently.⁶³⁻⁶⁴

The FN current density across an energy barrier ϕ under the effect of an electric field E is described by the FN equation and can be expressed as (Fig. 1.2)

$$J = \frac{1.54 \times 10^{-6} E^2}{\phi^2(y)} \exp\left[-6.87 \times 10^7 \frac{\phi^{2/3} v(y)}{E}\right] Acm^{-2} \quad (1.15)$$

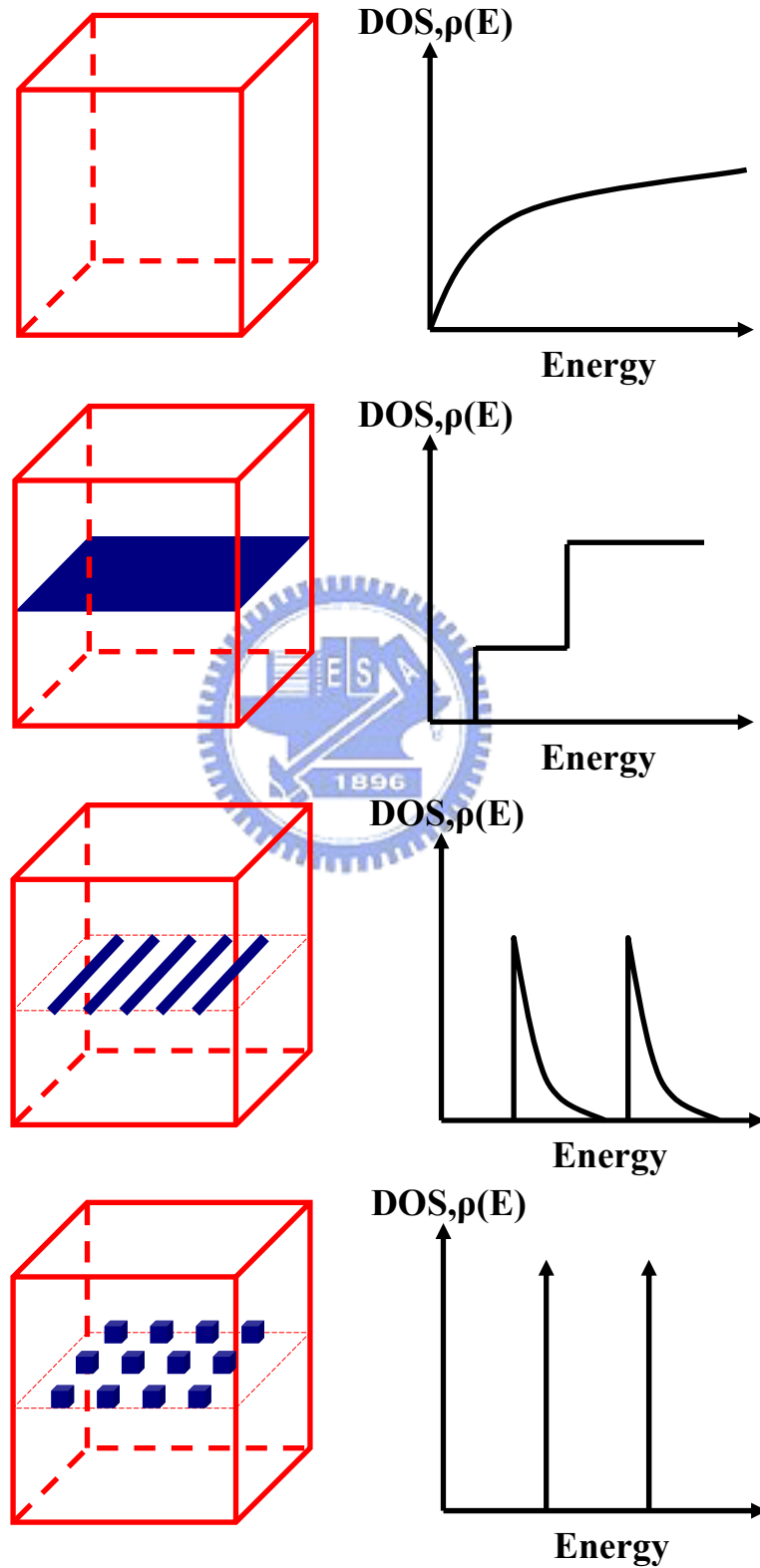


Figure 1.1 The nanostructure and their corresponding density of states.

where E is the applied electric field of the tip, ϕ is the work function (in eV), $t(y)$ and $v(y)$ are correction factors related to the electric field, and y can be approximated as

$$y = 3.79 \times 10^{-4} E^{1/2} / \phi \quad (1.16)$$

For simple, the factors $t^2(y) \approx 1$ and $v(y) = 0.95 - y^2 \approx 1$. The electric field at the tip can be represented as

$$E = \beta V_g \quad (1.17)$$

where β is the field enhancement factor, and V_g is the voltage applied to the gate and emitter electrodes. Thus, the current of the field emission array is

$$I = nAJ = nA \frac{1.54 \times 10^{-6} (\beta V_g)^2}{\phi} \exp \left[-6.87 \times 10^{-7} \frac{\phi^{3/2} v(y)}{\beta V_g} \right] \quad (1.18)$$

where n is the number of emitters and $A(\text{cm}^2)$ is the emission area per tip.

The logarithmic form of eq. (1.18) can be expressed as

$$\log \left(\frac{I}{V_g} \right) = \log \left(1.54 \times 10^{-6} \frac{nA\beta^2}{\phi} \right) - 2.98 \times 10^7 \frac{\phi^{3/2} v(y)}{\beta V_g} \quad (1.19)$$

Consequently, a plot of $\log(I/V_g^2)$ versus $1/V_g$ yields a straight line with

slope m and intercept b giving by following equations:

$$m = -2.84 \times 10^7 \left(\frac{\phi^{3/2}}{\beta} \right) \quad (1.20)$$

$$b = \log \left(1.4 \times 10^{-6} n\alpha \frac{\beta^2}{\phi} \exp \left(\frac{9.87}{\sqrt{\phi}} \right) \right) \quad (1.21)$$

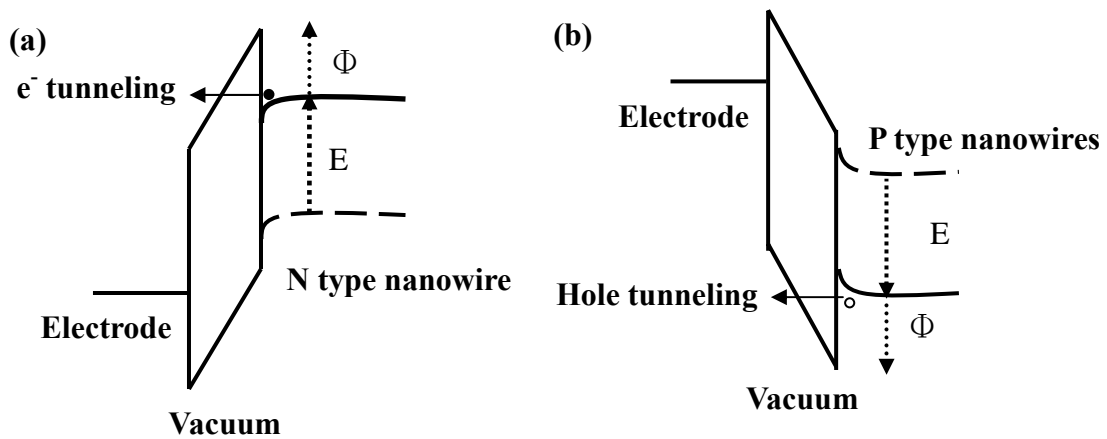


Figure 1.2 Energy band diagram for (a) n type nanowire and (b) p type nanowire in electric fields showing electron and hole tunneling, respectively.

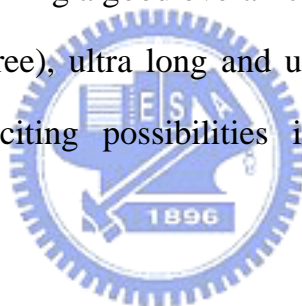
1.3 Nano Structure Fabricated of Material

The “top-down” chemical approaches⁶⁵ to high quality such as “T-wires” and “V-groove wires”⁶⁶ are combine lithography with epitaxial growth technology. “T-wires” have been synthesized by growing semiconductor quantum wells via molecular beam epitaxy (MBE), follow by cleavage and overgrowth on the cleaved surface, while “V-groove nanowires” have been fabricated by etching trenches on the surface and then deposited materials into the grooves. These nanowires synthesized by these methods are embedded in the substrates cannot assemble into complex devices.

Although nanowires can be fabricated using advanced lithography technologies, such as e-beam writing, proximal-probe patterning, and x-ray lithography. However, these methods are slow and high cost, the development of “bottom-up” technologies to rapidly synthesize large numbers of nanowires with low cost represent another important approach to nanowires. An important issue in the study and application of nanowires is how to control the size,

dimensionality, interfaces of these nanostructures and assemble them into two-dimensional and three-dimensional functional superstructures.

Since the discovery of carbon nanotubes (CNTs) in 1991, one-dimensional nanowires of elemental and compound semiconductors such as Si,⁶⁷⁻⁷⁰ Ge,⁷¹⁻⁷² InP,⁷³ GaAs⁷⁴ and SnO₂⁷⁵ have been synthesized by vapor-liquid-solid (VLS) growth mechanism,⁷⁶⁻⁷⁸ solution-liquid-solid (SLS) growth mechanism,⁷⁹ gas-solid (GS) growth mechanism,⁸⁰ laser-assisted catalytic growth (LCG),⁸¹ template-based synthetic approaches,⁸² physical vapor deposition (PVD),⁸³⁻⁸⁵ chemical vapor deposition (CVD)⁸⁶⁻⁸⁹ and oxide-assisted nucleation.⁹⁰⁻⁹¹ The ability to synthesized nanometer scale control in diameter during anisotropic crystal growth while maintaining a good overall crystallinity, large quantities of high pure (contamination-free), ultra long and uniform-sized nanowires from these techniques offer exciting possibilities in fundamental and applied research.



1.3.1 Vapor-Liquid-Solid (VLS) Growth Mechanism

Since the 1964, Si whiskers were synthesized by the well-known VLS growth mechanism (Fig. 1.7). In the VLS growth mechanism, metal particles such as Au, Fe, or Cu, are deposited on the Si substrate used as the mediating solvent.⁸⁴⁻⁸⁸ The Au forms the Au droplet on the Si substrate. The liquid droplets serve as catalytic sites, which absorb the reactants on the substrate. When droplets supersaturated, the reactants in vapor phase bond to the Si substrate at the liquid-solid interface, and the nanowires grow. The growth directions of these nanowires are decided by the lowest liquid-solid interfacial energy at the liquid-solid interface.

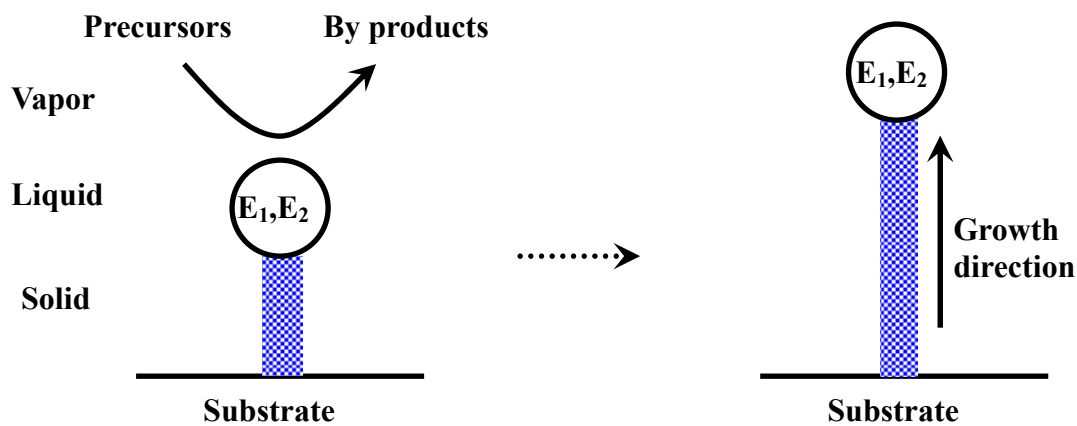


Figure 1.3 The VLS growth mechanism: the droplet is a metal such as Au, Ag, Pd, Pt, Ni, or Cu, and E₁ and E₂ are elements of the crystal phase dissolved in the metallic flux droplet.

Since the method is originally applied with the liquid metal drops, the minimum of the wires diameter is determined by the diameter of the droplet at the tip.⁸⁹ The observation related to the thermodynamic limit for the minimum radius of the alloy droplets at high temperature

$$r_{\min} = \frac{2\sigma_{LV}V_L}{RT \ln s} \quad (1.22)$$

where σ_{LV} is the liquid-vapor surface free energy, V_L is the molar volume of liquid, and s is the vapor-phase supersaturation. Therefore, monodisperse nanowires can be synthesized by applying single size metal clusters mediate as catalysts for nanowires growth. Most of the techniques related to the VLS process, the catalyst usually in the nanowires and may affect its intrinsic properties.

1.3.2 Solution-Liquid-Solid (SLS) Growth Mechanism

The SLS growth mechanism⁹² (Fig. 1.4) shows that processes analogous to

VLS growth can operate at low temperature. The fibers or whiskers prepared by SLS mechanism have diameters of 10 to 150 nanometers and lengths of several micrometers. For example, methanolysis{t-Bu₂In[μ-P(SiMe₃)₂]}₂ in aromatic solvents gives highly crystalline InP fibers (dimension 10 - 100 nm × 50 - 1000 nm) at temperature as low as 111 - 203 °C. In this growth mechanism, the reactant dissolve in the solvents resulting (InP)_n fragment absorbed by the molten In droplets and crystallize as the InP nanowires. The defect-free Si nanowires (Fig. 1.5) also synthesized by the SLS growth mechanism. In the process, solvent-dispersed alkanethiol-capped gold nanocrystals catalyze Si nanowires growth at temperature 500°C and 270 bar.

In the SLS growth mechanism, crystal growth requires (1) a reversible pathway between the fluid (solution, melt or vapor) and the solid phase or (2) high surface mobility in the solid phase. These conditions let the atoms, ions, or molecules to get the correct position developing the crystal lattices. Ionic and molecular solids can be crystallized from solution at low temperature because aqueous or organic solvents dissolve their constituent ions or molecules and condition (1) is met. However, covalent nonmolecular solid such as III-V semiconductors are generally insoluble cannot be crystallized from the solution at low temperature. These materials should be synthesized from solution by condition (2) with two circumstances that support low-temperature crystal growth: catalysis by protic reagents and the participation of metallic flux particles. The low-temperature SLS growth mechanism shown in Fig. 1.4 is analogous to the high-temperature VLS growth mechanism, and the SLS growth mechanism possibly opening the low temperature method to synthesize many covalent solids such as fibers, whiskers, and quantum dots.

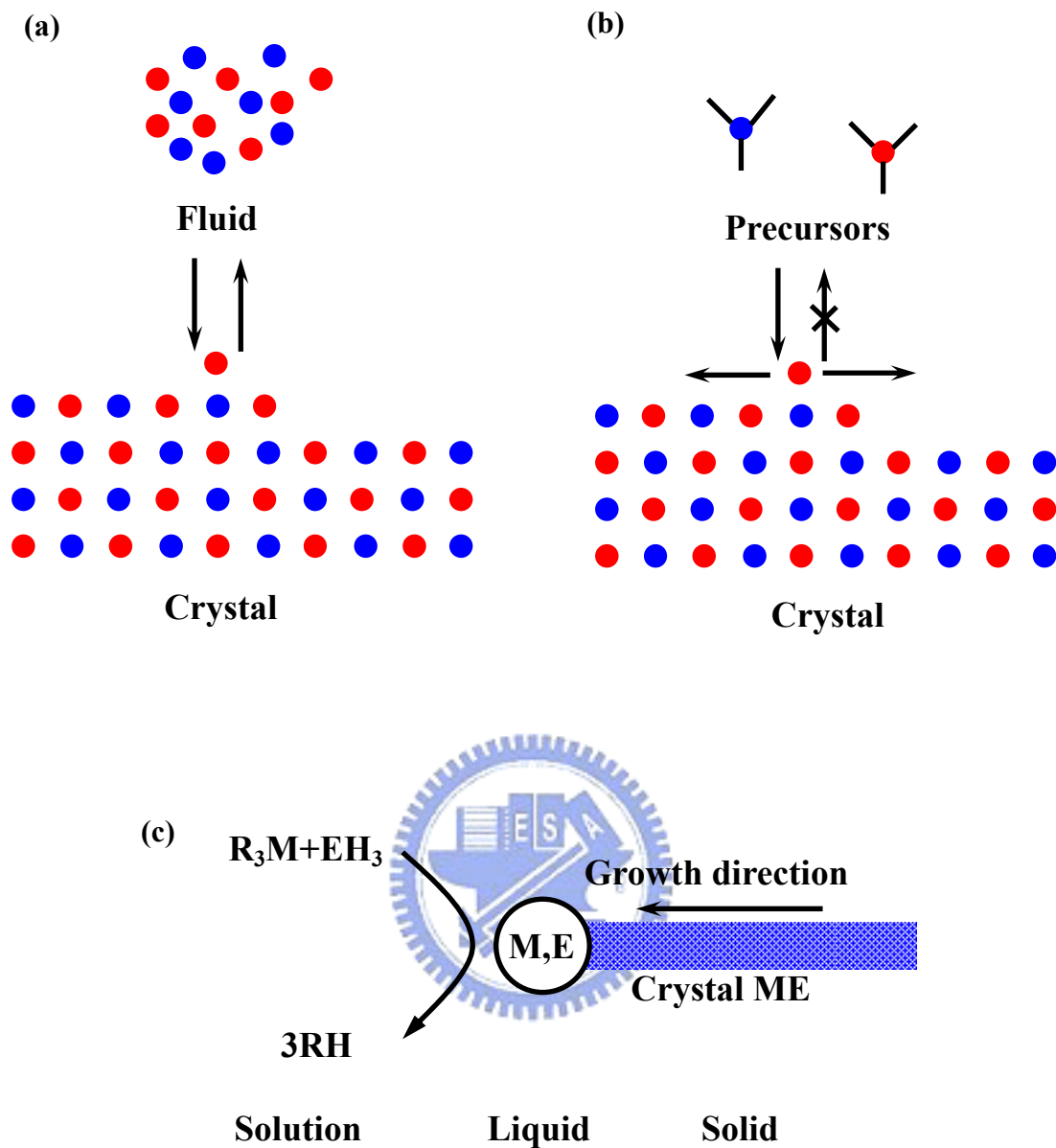


Figure 1.4 Crystal growth pathway: (a) growth by reversible deposition from solution, liquid or vapor [condition (1)] (b) growth by irreversible deposition with high solid-phase atomic mobility [condition (2)] (c) SLS mechanism: the flux droplet is In, M and E are elements dissolved in the flux droplet. The crystalline fiber and attached flux droplet are suspended in the solution.

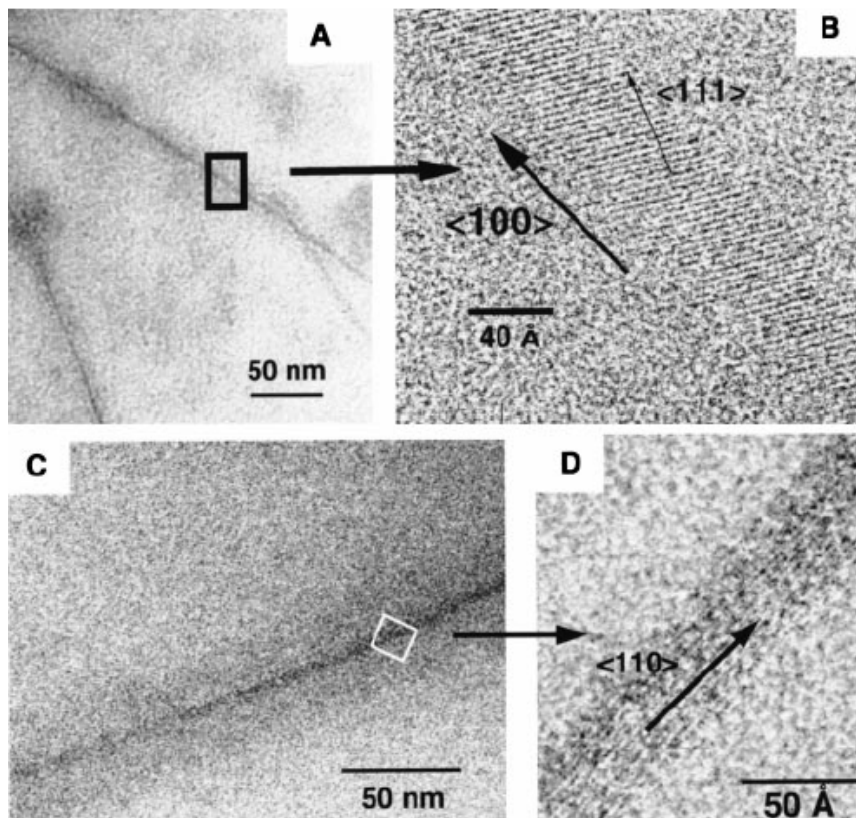


Figure 1.5 The Si nanowires growth by SLS mechanism.

1.3.3 Laser-Assisted Catalytic Growth (LCG)

Compared with the classical VLS growth mechanism, nanoparticles of metal or metal silicide in large quantity are rather easy obtained from the laser ablation method using metal-containing target. The typical experiment was carried out by using excimer laser to ablate the target in an evacuated quartz tube filled with argon gas in which the pressure and temperature are varied (Fig.1.10). The solid target could be high pure powder mixed with metals (Fe, Ni, or Co). The background pressure is used to control condensation and cluster size, while the temperature can be varied to maintain the catalyst cluster in the liquid state.

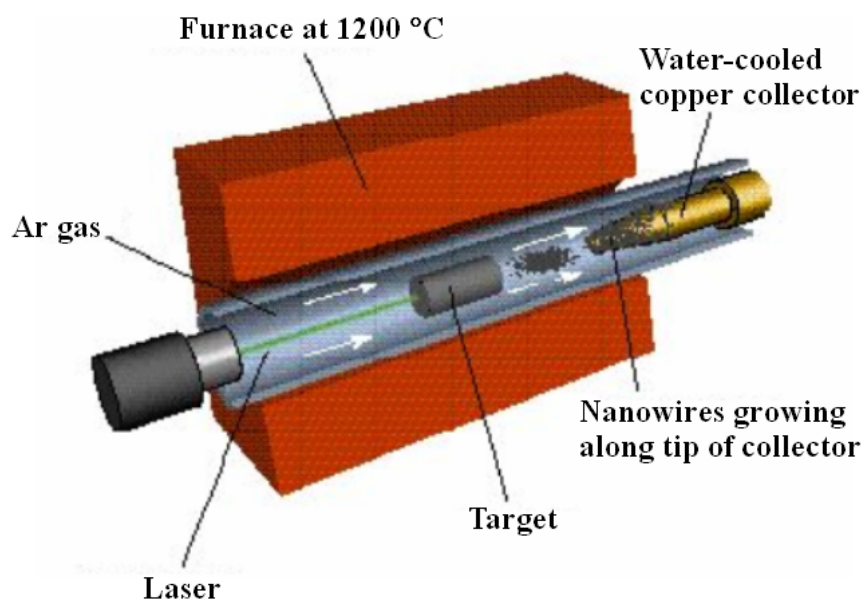


Figure 1.6 Schematic of the LCG growth apparatus.

Nanowires growth initiates after a laser-generated cluster becomes supersaturated and stopped when the nanowires and attached liquid cluster go through the hot zone of the furnace as shown in Fig. 1.6. These variations result in deviation of the mean diameter of the nanowires, and the nanowires produced in this method with broad diameter distribution. In contrast to the VLS growth mechanism, those 1D materials grown by the LCG mechanism (Fig. 1.7) often have some structure defects, such as the stacking faults, interface roughness, grain boundary, twins, etc.

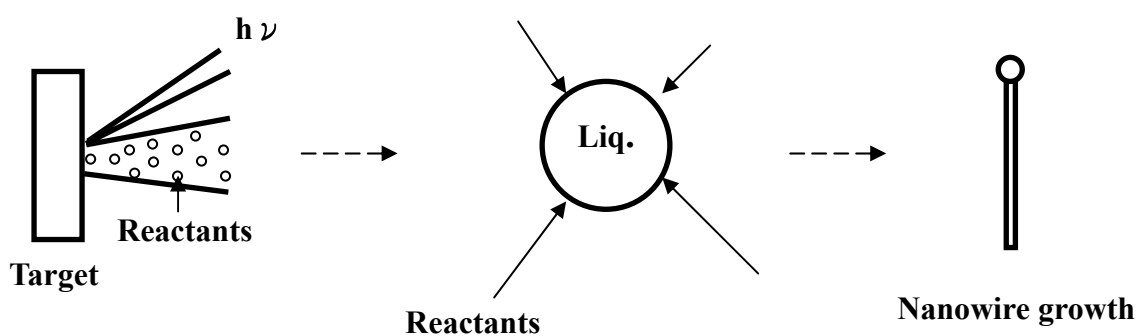


Figure 1.7 The LCG growth mechanism.

1.3.4 Template-Based Synthetic Approaches

Recently, template-based synthesis that used zeolites, membranes, or nanotubes can control growth of nanowires but usually form the polycrystalline materials.⁹⁴⁻⁹⁵ Template-based synthesis is a convenient method for nanowires growth. These templates have nanoscale channels within mesoporous materials,⁹⁶ porous alumina,⁹⁷ carbon nanotubes⁹⁸⁻¹⁰⁰ and polycarbonate membranes.⁴⁹ This method is used to prepared nanowires,¹⁰¹ nanotubes¹⁰²⁻¹⁰³ composed of electronically conductive polymers,¹⁰⁴ metals,¹⁰⁵⁻¹⁰⁶ semiconductors,^{95,106} and many other materials.^{48,107-110} Besides, these pores in the membranes have monodispersed diameters, analogous monodispersed nanostructure can be obtained.

A number of membranes have been used in this type of template process. Take the anodic alumina membranes (AAM) as an example, a self-assembled nano-porous material formed by anodization of Al in an appropriate acid solution has draw interest as their several unique structure properties such as controllable pore diameter, extremely narrow size distribution for pores diameter and their interval, ideally cylindrical shape of pores. They have been used to fabricated nanosized fibers, nanorods, nanowires, and nanotubes of metals, semiconductors and other solid materials. The AAM occupied hexagonal ordered porous structure with the porous diameters ranging from 10 to 200 nm, porous density in the range 10^{10} - $10^{12}/\text{cm}^2$, and high aspect ratio of the channel, which is difficult to achieve with conventional lithography technology.

After fabricating the AAM template, nanowires can be growth in these nanopores by four methods: (1) Electrochemical deposition of metals, alloys

and compounds into the pore of the template; (2) Electrophoretic filling of the pores with colloids; (3) Filling with sol-gel; (4) Filling through CVD or VLS growth mechanism.¹⁰⁹⁻¹¹⁴ Using AAM, the different kinds of ordered nanowires array have been synthesized. All of these methods are powerful techniques to prepare nanowires of various compositions can provide good control over the length and diameter of nanowires. Expect the VLS growth combines with the template-based method; other methods have the draw back that they often produce polycrystalline materials, which are less suitable for both fundamental and applied studies.

1.4 Characteristics of Zinc Oxide

The material ZnO is a direct-band-gap semiconductor (3.37 eV) with large exciton binding energy (60 meV), which is of interest for short-wavelength light-emitting electrooptical nanodevices. Many previous studies focus on the preparations and electrical properties of the ZnO films.¹¹¹⁻¹³⁰ Very recently, ZnO NWs (Fig. 1.12), which synthesized by Yang's group¹³¹⁻¹³⁴ have been a subject of particular attention; they can be grown in single crystal form, achieve high aspect ratios, exhibit quantum confinement effects at sufficiently small diameters and emit ultraviolet (UV) laser, which can be used in luminescent device applications.^{64,135-148}

ZnO NWs for optical application are usually prepared on the sapphire substrate by the VLS growth mechanism. However, due to the insulating characteristic of sapphire substrate, it is not suitable for the electrooptical application. In order to develop the electrooptical application, the Si substrate was used to be the substrate. A rarely catalyst, Cu, was adopted to synthesize

ZnO NWs, and a new method was used to enhance optical properties of ZnO NWs in later sections. In addition to the good optical characteristic, monophasic powder of high crystallinity, narrow particle size distribution and fine particles size were successfully prepared in short reaction time compared to the previous VLS studies.

1.5 Research Objectives of Dissertation

About the study for ZnO NWs, we give consideration to material characteristics and potential application in the future especially in the field emission display devices of NWs. Through adjust growth temperature at the VLS process to optimize the better precipitation environment in the horizontal furnace. While the different carrier gas flowing rates will change the concentration or density of Zn vapor on the two step VLS process.

The different catalyst, copper and gold, will affect the morphology and geometry of the ZnO NWs. Besides, in the first thermal process at two step VLS process the distinct eutectic temperature from substrate and catalyst will appear individual morphology and crystalline before second thermal process in this study. The later section will discuss the relationship with growth mechanism and status of these different catalysts.

Through optical analysis, photoluminescence measurement, the typically optical emission characteristics will be analysis to judge the lattice structure of the ZnO NWs. The optical band gap shift also offer us there are how much impurities into the ZnO NWs while in the VLS process. Furthermore, to improve the field emission ability the Sn dopant is introduced. While the Sn diffuse into the ZnO NWs, the optical emission have more emission because

the Sn atom generate a temperately optical band gap which cause two step electron jumping.

According the properties of the field emission of the ZnO NWs, it is more concerned with the turn-on electric field and emission current density of the ZnO NWs field emission array. The previous reports can push the turn-on electric field to about 6-8 V/ μm while the emission current density is locate around 1 mA./cm². Through the two step VLS process and precisely carrier gas controlled, the turn-on electric field and emission current of the ZnO NWs are made more excellence. The Sn dopant introduced which make to scale new heights for the characteristics of the Sn dopped ZnO NWs. This details will discussion at the least section.

On the least, the lithography technology is success fabricated a gate controlled ZnO field emission triode devices. The gate voltage is effectively control the turn-on electric field and emission current density. This prototype presents the potentials of the ZnO NWs in the field emission display application in the future.