

CHAPTER 1

INTRODUCTION TO ZINC OXIDE AND OVERVIEW OF NANOWIRES

The unique properties of zinc oxide (ZnO) and its potential applications have been highlighted in this chapter. In addition, an importance of one-dimensional (1-D) nanostructures (NSs) especially nanowires (NWs) as a fundamental building blocks for future nanoscale devices and their growth mechanism have been briefly discussed. Besides, the growth of ZnO NSs by radio frequency magnetron sputtering has also been reviewed.

1.1 Introduction to ZnO

Semiconducting materials with wide band gap have attracted a tremendous attention in various applications such as electronics, optoelectronics, photocatalysis, and sensors due to their unique properties. Among the various wide band gap semiconducting materials, ZnO is one of the compound semiconductors that has been intensively studied for optoelectronic applications due to its intrinsic properties namely direct and wide band gap (3.37 eV) with large exciton binding energy (60 meV). It is considered as a promising material for the fabrication of light emitting and laser diodes in the ultraviolet (UV) and blue spectral region. Further, it is a potentially competing material to gallium nitride (GaN) for the fabrication of optoelectronic devices due to its large exciton binding energy and high thermal stability at room temperature. Some of the basic properties of ZnO will be discussed briefly in the following sections.

1.1.1 Crystal and surface structure of ZnO

ZnO is one of the II-VI compound semiconductors whose ionicity resides at the borderline between covalent and ionic semiconductors. At ambient pressure and temperature, ZnO crystallizes in the wurtzite structure as shown in Fig. 1.1. This is a hexagonal lattice belonging to the space group $P6_3mc$ and is

characterized by two interconnecting sublattices of Zn^{2+} and O^{2-} , such that each Zn ion is surrounded by a tetrahedral O ions and vice-versa.

Additional to the wurtzite phase, ZnO is also known to crystallize in the cubic zinc blende and rocksalt structures. Zinc blende ZnO is stable only by growth on cubic structures [1] whilst the rocksalt structure is a high-pressure meta-stable phase forming at ~ 10 GPa and cannot be epitaxially stabilized [2]. Theoretical calculations indicate that a fourth phase cubic cesium chloride may be possible at extremely high temperatures. However, this phase has yet to be experimentally observed [3].

ZnO with wurtzite structure has the characteristics of non-centro symmetry with polar surfaces where positively charged Zn planes (0001) and negatively charged O planes (000 $\bar{1}$) are arranged alternatively layer-by-layer along the c-plane. Due to the anisotropic property of ZnO, the surface energy varies according to the polar and non-polar nature of the surfaces. The surface energies of the polar c-plane (0001), non-polar m-plane (1010) and non-polar a-plane (1120) are 2.0, 1.15 and 1.25 J/m² respectively [4, 5]. This anisotropy is very important factor on the growth of NSs that leads to the preferential growth of ZnO along the c-axis as there will be preferential atom/molecule incorporation on the polar faces rather than non-polar faces.

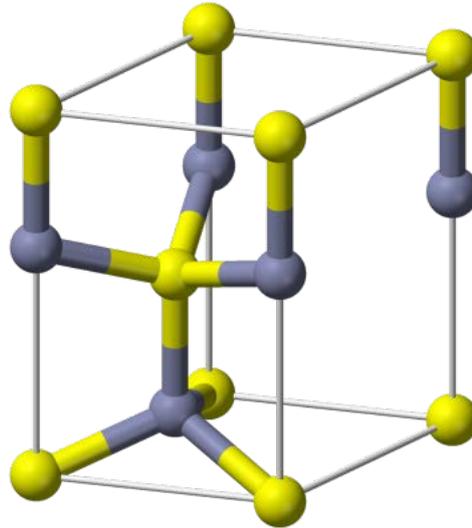


Fig. 1.1 Hexagonal wurtzite crystal structure of ZnO (O and Zn atoms are shown as yellow and grey spheres respectively).

1.1.2 Physical properties of wurtzite ZnO [6]

Properties	ZnO
Band gap, E_g [eV]	3.37, Direct
Exciton binding energy [meV]	60
Lattice constants, a_0 [Å]	3.2469
c_0 [Å]	5.2069
Density (g/cm^3)	5.606
Melting point (K)	2248
Electron effective mass, m_e [m_0]	0.24
Electron mobility, [$\text{cm}^2\text{V}^{-1}\text{S}^{-1}$]	200
Hole effective mass, m_h [m_0]	0.59
Hole mobility, [$\text{cm}^2\text{V}^{-1}\text{S}^{-1}$]	5-50

1.1.3 Potential applications

ZnO is one of the promising materials for the fabrication of optoelectronic devices such as light emitting and laser diodes in the UV/blue spectral region of the electromagnetic spectrum due to its wide and direct band gap with large exciton binding energy at room temperature. The exciton binding energy is much larger than that of GaN (25 meV). The thermal energy at room temperature (26 meV) ensures an efficient exciton emission at room temperature under low excitation energy. The conventional planar light emitting diodes (LEDs) [7] suffer from the total internal reflection which results low quantum efficiency. Hence, a hybrid n-ZnO NWs/p-GaN thin film or n-ZnO NWs/p-Si substrate heterostructures can be utilized to increase the extraction efficiency of the LEDs by virtue of the wave-guiding properties of the NWs. However, the quality of the NWs may be restricted by the lattice and thermal mismatch between ZnO and substrate material. This can be overcome by fabricating the LEDs from NW based lateral and core/shell p-n junctions [8] and other hybrid structures [9] which are interesting as well for laser applications.

ZnO is one of the diamagnetic materials in its bulk form. However, it exhibits room temperature ferromagnetic behavior at reduced dimensionalities due to the size effects along with surface defects and vacancies. Therefore, it has triggered a considerable interest in the field of spintronics which could pave the way to use spin in addition to charge in semiconductor devices [10].

ZnO NSs is a most promising material for the fabrication of solid state chemical sensors due to their small dimension, low cost, low power consumption and high compatibility with microelectronic processing. The fundamental sensing mechanism of resistance based ZnO gas sensors relies on a change in electrical conductivity due to the process of interaction between the surface complexes such as O^- , O_2^- , H^+ and OH^- reactive chemical species and the gas molecules to be detected. Hence, ZnO NSs has been utilized as a gas sensing

material for the detection of hazardous gases in chemical process controlling and toxic environmental monitoring due to the dramatic change in the electrical resistance by the presence of reactive gas in air [11,12]. Thus, it has been widely studied as a sensor. Further, ZnO being a bio-safe and biocompatible material, it can be directly interfaced to the bio-molecules for the versatile applications in life-sciences [13,14].

ZnO has received a great attention as a photocatalyst for the degradation and mineralization of environmental pollutants due to its wide band gap and low cost [15]. Hence, it is an efficient photocatalyst and comparable to the benchmark of TiO₂. In general, the photochemical reactions take place only at the surfaces of the catalyst. Therefore, 1-D form of ZnO NSs is emerging as a potential candidate for enhanced photocatalytic applications under the irradiation of UV light. Further, it can be used to generate hydrogen by water splitting and synthesize H₂O₂.

Hence, the fabrication of 1-D ZnO NSs has received a great deal of research interest by various deposition techniques such as thermal evaporation, electron beam evaporation, chemical vapor deposition, metal organic chemical vapor deposition, magnetron sputtering, pulsed laser deposition and hydrothermal process [16-22]. Among the various deposition techniques, the sputtering is one of the least investigated techniques for the fabrication of ZnO NSs since it is typically engaged for the deposition of thin films. Hence, we have focused our attention on the fabrication of 1-D ZnO NSs without any external catalyst by radio frequency (RF) magnetron sputtering.

1.2 Nanowires: An overview

Ever since the discovery of carbon nanotubes by Iijima [23], there has been great interest in the fabrication and characterization of other 1-D NSs such as NWs and nanorods (NRs). 1-D NSs are characterized by their diameters in the sub-one hundred nanometer scale and lengths ranging from several hundreds of

nm to as high as a few cm. Due to their nanoscale dimensions in the radial direction, they have size confinement effects which give the novel physical properties as compared to bulk materials. Their 1-D geometry on the nanometer scale provides an extremely high surface to volume area with a nanoscale radius of curvature and great mechanical flexibility with near theoretical strength. Another important feature of NWs is that its small footprints on the large lattice and thermal mismatched substrates can facilitate the fabrication of heterostructures without creating dislocations. This advantage over planar structures provides an unprecedented flexibility to create a broad range of structures with a combination of different materials that may lead to the observation of exciting physical phenomena or novel functionalities for applications. In particular, NWs may pave the way for the integration of microelectronic devices on silicon with optoelectronic and photonic devices based on compound semiconductors [24]. These properties are advantageous in many chemical and mechanical applications. The geometry also provides anisotropic properties. Their length, reaching as high as the cm scale, makes them easy to manipulate for device fabrication [25].

NWs are promising materials for advanced optoelectronic applications. In addition to the unique aspects of their physical, chemical, and mechanical properties, the size of these materials is comparable to visible light in wavelength from 400 to 650 nm. This implies that NWs can be used to handle light on a nanometer scale and thus can be used as building blocks for the next generation optoelectronic applications. Indeed, novel methods of the manipulation of light with NWs, including nanoscale Fabry–Perrot mode stimulated emission, wave guiding of photons, random lasing action, highly efficient luminescence, and extremely sensitive photo-detection, have recently been demonstrated. The concept of many advanced NWs based optoelectronic devices including light-emitting diodes (LEDs), lasers, optical sensors, photodiodes, and photovoltaic cells have also been demonstrated.

The physical and chemical states of NWs dominate their optical properties. The length and diameter of NWs as well as their alignment affect the emission and absorption properties. The composition, impurity or doping level, defect concentration, crystal structure, growth direction and nature of the facets are also critical to the emission and absorption. It should be noted that these physical and chemical states are closely related to the growth of NWs. Therefore, one must fully understand the growth behavior of NWs and develop rational and reliable growth processes to exploit the potential of NWs in optoelectronics.

NWs are a result of anisotropic, 1-D crystal growth on a nanometer scale. Therefore, the key issue related to the growth of NWs is how to induce 1-D crystal growth in a controlled manner. Regarding this, many approaches have been studied including the use of the metal-catalyst-assisted vapor–liquid–solid (VLS) and vapor–solid (VS) mechanisms that are briefly discussed in the following section.

1.3 Growth of NWs

Up to now, many techniques have been employed for the fabrication of NWs. In general, the growth of NWs can be described by two different approaches.

- i) Top-down approach
- ii) Bottom-up approach

Top-down approach

A top-down approach that combines multiple lithographic steps and anisotropic chemical etching processes, to fabricate NWs with controlled properties along their longitudinal and transverse axes. It is perhaps the most actively engaged route for commercial applications. Further, this approach has only been recently enabled by developments in sub-micron lithography, the

potential for seamless integration makes it very compatible with mass production needed for commercial viable technologies.

Despite the possibilities of this technology, it is fundamentally restricted in terms of future physical and economical limits. Since epitaxy technologies are done in a layer-by-layer fashion, this leaves traditional lithography incapable of making 1-D structures. Some groups have had succeed with opening a matrix of holes in a dielectric and subsequently growing epitaxially in selective areas [26]. These groups also take advantage of a small growth window (patterned) which allows for primarily vertical pillar growth instead of lateral. However, despite some success with this combinational approach, the small processing window makes growth in these structures extremely difficult.

Bottom-up approach

The limitations of top-down approach can be overcome by the bottom-up. Several synthetic bottom-up approaches can be utilized to prepare 1-D NSs. Among them, the vapor phase synthesis is the primary and widely used method for fabricating NWs in a number of materials systems. This vapor phase synthesis is generally divided into two categories; physical vapor deposition (PVD) and chemical vapor deposition (CVD). In PVD, the source material is directly vaporized and reassembled into a NW without changing the basic chemical components of the starting material. On the other hand, CVD involves a chemical change occurring in the vapor phase where the possibility of chemical reactions between source materials in the form of vapors with the gases introduced separately into the dynamical system at elevated temperature. Overall, one can obtain controlled and high quality NWs using vapor phase techniques as compared to the other wet chemical methods. It is essential to understand the growth mechanisms which are utilized in vapor phase synthesis to control the orientation and quality of the NWs. There are a variety of growth mechanisms such as VLS and VS reported for the unidirectional NWs growth [27].

1.3.1 VLS mechanism

VLS mechanism, which was first formulated in 1964 by Wagner and Ellis at Bell laboratories to explain the growth of elemental micrometer-sized Si whiskers, is a very useful route for the fabrication of NWs and many other NSs. It involves various intervening processes which differ from case to case, thus it allows a versatile design of the routes for the growth of NWs of different compositions and geometry. As the name ‘vapor-liquid-solid’ suggests three phases are involved in NW growth as shown in Fig. 1.2. VLS growth of 1-D materials involves three sequential steps [28].

1. Selective and rapid dissolution of solutes of interest from the gas phase into molten metal droplet (vapor-liquid interface)
2. Diffusional processes of solute through and on the surface of the droplet (liquid-solid interface) that establish supersaturation and
3. Precipitation of solute from molten metal droplet at the substrate-droplet interface (liquid-solid interface).

In general, VLS process begins with the deposition of a thin noble metal catalyst layer on desired crystalline substrate. By heating the metal catalyst under vacuum at above the eutectic point, an alloy is formed with the substrate materials. The formation of a eutectic turns the seed particle from a solid into a liquid, following the binary phase diagrams of the different material systems. Subsequently, by continuous supply of precursor materials from the vapor phase, the liquid droplets on the surface of the substrate saturate and eventually reach supersaturation. If the supersaturation is sufficient, crystal nucleation starts at the droplet-substrate interface. The (solid) wire grows layer-by-layer lifting the metal particle. During growth, there is a dynamic equilibrium between *supply* of materials from the gas phase, *transport* of materials through the droplet, and crystal *growth* at the droplet-NW crystal interface. Therefore, various thermodynamical and physiochemical factors may play a decisive role in determining the final product of the method.

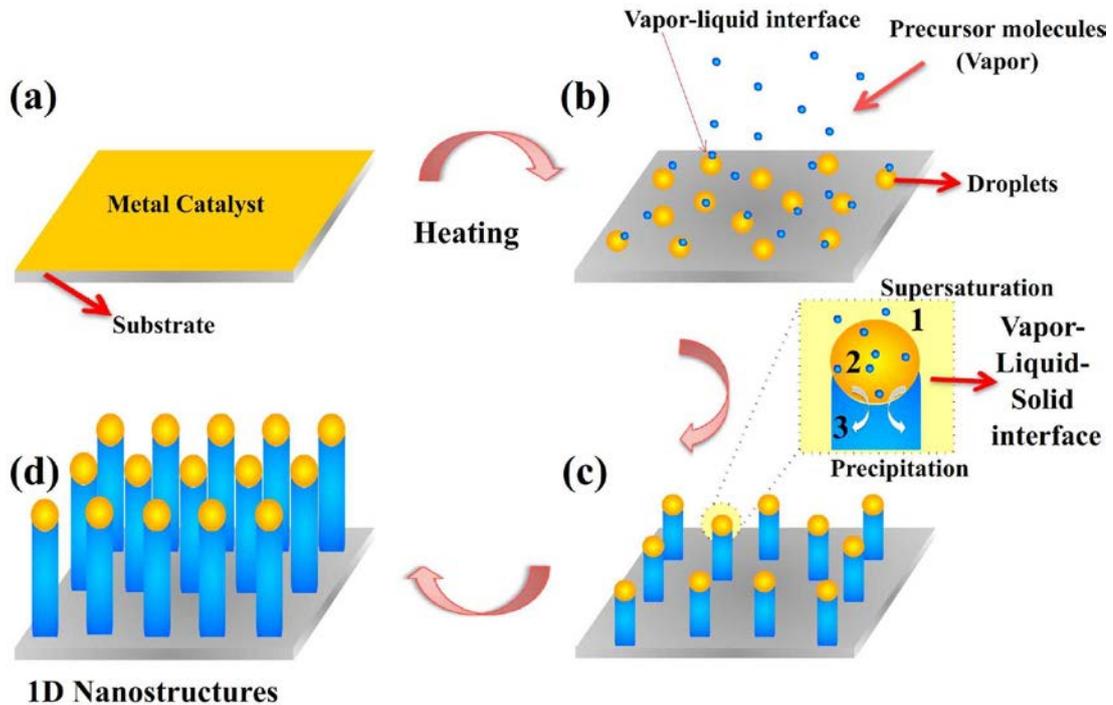


Fig. 1.2 Schematic illustration of NW growth by VLS approach. The inset at (c) denotes the step by step process involved in VLS mechanism; 1. Decomposition of semiconductor precursor at the vapor-liquid interface, 2. Diffusion through the metal catalyst/semiconductor metal liquid and 3. NW growth by incorporation of atoms into the growing liquid-solid interface of the NWs.

In VLS mechanism, precursors from the vapor phase first land on the surface of the catalyst droplet and then diffuse via hopping of individual atoms across the surface or through the bulk. Thus, the NW growth rate hangs on the concentration gradient and liquid catalyst at the tip of NWs enhances the growth rate of anisotropic NWs. The catalyst particle determines size along with position and density of the NWs. Mass transport via surface can lead to a larger growth rate, thus favorable for the fast production of NWs. This mechanism is widely used to realize the precise control of morphology including diameter and in situ doping while providing high quality single crystal NWs. Variety of materials including single and compound semiconductors from the group IV, III–V, and II–VI systems can be grown using this VLS mechanism by choosing a suitable metal catalyst.

1.3.2 VS mechanism

The VS growth mechanism is also used to grow variety of semiconducting NWs. This process occurs under similar conditions to VLS growth, however, without the aid of a catalyst. The step-by-step process occurs in VS mechanism is shown in Fig. 1.3. It is believed that the source of VS nucleation and growth may occur due to the high energy defects on the substrate or grain boundaries formed by the epitaxial deposition prior to the NW growth. Whereas, in the case of VLS mechanism due to the aid of catalyst, intentional and unintentional incorporation of impurities into the NWs happened strongly influence on the performance of electronic devices [29]. Growth in VS mechanism is observed to occur by ledge propagation where the nucleation of each new ledge was the rate limiting step. Though compared to VLS mechanism, the growth rate of VS mechanism is slow; it is possible to obtain high quality NWs by controlling the growth parameters such as temperature, vapor pressure, and so on. The reduced rates can be attributed to slower precursor decomposition kinetics, diffusion through a solid rather than a liquid, and/or slower atomic incorporation at sub-eutectic temperatures resulting weaker vapor-solid reactivity. In general, the VS mechanism is the driving force behind the synthesis of many kinds of architectures and hierarchical NSs, such as tetrapods, nanotubes, nanoneedles, nanohelices and nanosprings, nanorings, nanodisks, nanobridges and nanonails, nanopins, nanocombs, nanoflowers, nanowalls and so forth [30]. VS growth of silicon NWs was first reported in 2000 when Kamins et al. utilized CVD deposited Ti as the metal catalyst with either SiH_4 or SiCl_2H_2 as the silicon precursors.

In the above growth mechanisms, the VLS is perhaps the most widely used growth mechanism for the fabrication of 1-D NSs in which the metal catalysts such as Au and Ni are used to assist the fabrication of 1-D NSs. However, some issues such as incorporation of metal catalyst and structural modulation have to be addressed before the potential of NSs can be exploited in

the area of optoelectronics. During the growth, the metal catalyst inevitably becomes contaminated into the NSs as a result of contact between the liquid alloy and the semiconductor at a high temperature [31]. This contamination can increase the impurity level in the band gap and thus degrade the optical properties of NWs. Hence, an alternative approach is essential for the fabrication of NSs without any external catalyst which is possible by VS growth approach. Therefore, the VS growth approach has received a great attention for the fabrication of high quality 1-D NSs.

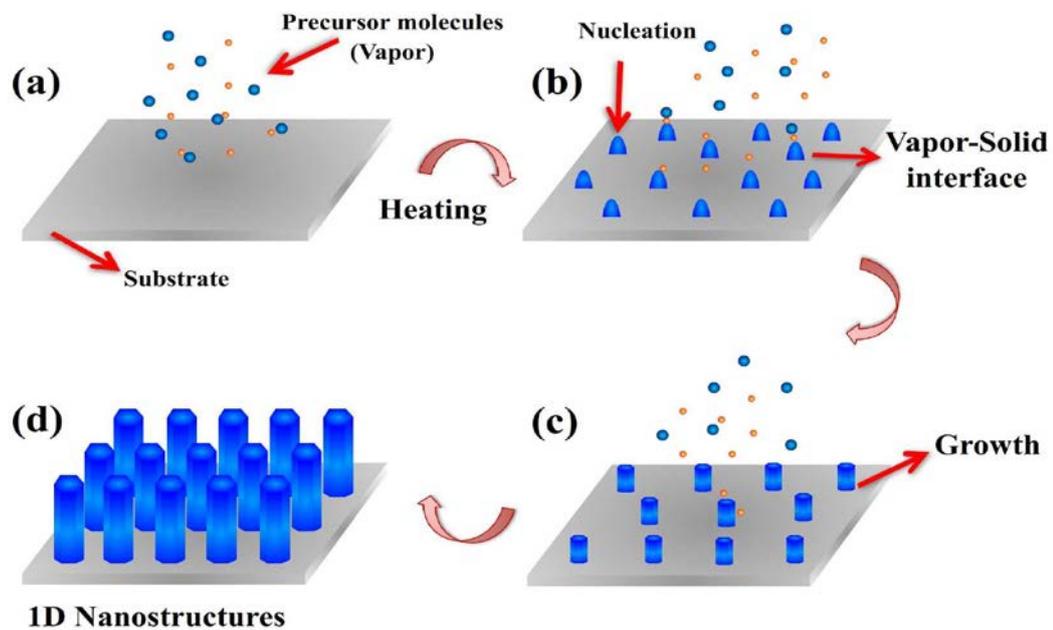


Fig. 1.3. Schematic representation of NWs growth by VS approach.

1.4 Motivation of thesis

Sputtering is one of the controlled deposition techniques in terms of scale-up and mass production which makes it an effective economic approach for the industrial applications [32]. Hence, many research groups have paid their attention on the growth of 1-D NSs using magnetron sputtering due to its

excellent properties of materials since the growth was carried out under vacuum condition [33-37].

In recent years, J. M. Ting et. al., investigated the growth of 1-D ZnO NSs on various substrates such as silicon and sodalime glass (corning 1737F) coated with a thin Ti as a adhesive layer and then with electroless plated copper as a catalyst [20,38-44]. The growth follows the catalytic assisted VLS approach. Further, it was also observed that the crystalline nature of the NWs is enhanced from polycrystalline to single crystalline by the introduction of oxygen into the chamber, but no visible changes were noticed on the surface morphology of the NWs [38]. However, in the above growth approach, the growth of 1-D NSs is initiated by the interfacial layer or catalyst. It is obvious that the interfacial layer or catalyst is an undesirable external impurity which will affect the quality of the NSs by incorporating into the growing lattice. Hence, the performance of the devices fabricated using these NSs will be deteriorated [45,46]. Therefore, the growth of 1-D ZnO NSs without any catalyst as well as interlayer is important for certain applications. Hence, the researchers are motivated to fabricate the 1-D ZnO NSs without any external catalyst, termed as VS growth approach.

Nevertheless, Choopun et. al., have attempted to fabricate ZnO NSs on copper and quartz substrates by RF magnetron sputtering. However, the NSs are coalescenced with each other and not vertically aligned on the substrates [47-48]. In addition to this, it was reported that the evolution of NSs such as NWs and nanobelts depends on the deposition rate of the materials [48].

Recently, S. W. Kang et. al., realized the vertically aligned Ga doped ZnO NRs at elevated substrate temperatures on silicon substrates with different buffer layer thickness by magnetron sputtering [49]. However, the cross sectional view of SEM image clearly represents the coalescenced nature of the NRs. The buffer layer also introduces strain in NRs. Therefore, the same group grew the NRs without buffer layer and achieved the vertically aligned Ga doped ZnO NRs on

sapphire substrates without using the low temperature buffer layers [50]. Further, they concluded that the incorporation of Ga dopants was promoted the formation of vertically aligned NRs by inducing the island growth in the initial stage since they were obtained thin film like morphology in undoped ZnO under identical growth conditions.

Based on the earlier reports, X. M. Wu et. al., grew ZnO NSs and achieved the vertically well aligned transition metals such as Cu, Mn and Cr doped ZnO NRs on silicon and quartz substrates by RF magnetron sputtering. However, the NRs are coalesced as evidenced from the cross sectional SEM images [51-53]. They were also reported that the room temperature ferromagnetism in transition metals doped ZnO NRs was only attributed to the exchange coupling of the dopants and not by the bound magnetic polarons (defect mediated mechanisms).

From the review of literature, it is clearly observed that vertically aligned ZnO NSs such as NWs and NRs yet to be fabricated by RF magnetron sputtering without external catalyst. Therefore, it has been motivated to fabricate 1-D ZnO NSs without metal catalyst by varying the growth parameters particularly substrate temperature and pressure.

1.5 Summary

This chapter discusses the importance of ZnO in the context of optoelectronic applications due to its intrinsic properties. The stable crystal structure and role of surface energies on the anisotropic growth of ZnO NSs has also been discussed. Further, we have focused on the physical properties and potential applications of ZnO. The need for the fabrication of semiconducting ZnO NSs to overcome the limitations in planar device has also been discussed. Second part of this chapter illustrates an overview of semiconductor NWs. Over past decade, 1-D growth with superior control in structure, dimension and spatial alignment becomes more and more important. The possible growth mechanism such as VLS and VS for the fabrication of semiconductor NWs was added in the chapter. Finally, the need of VS growth mechanism has been explained for the growth of semiconductor NWs over the VLS catalyst approach. Besides, the motivation of the thesis has been added to the current understanding of the ZnO NSs by RF magnetron sputtering technique.