Chapter 1
Introduction

Over the past decades, the understanding of semiconductor nanowires (NWs) and nanobelts (NBs) have contributed significantly in the development of nanotechnology. In fact, these are among the most attractive class of materials for functional nanodevices, including gas and biological sensors (Pearton *et al*., 2010; Li, Z *et al.* 2009), field effect transistor (Boyd & Brown, 2009), light emitting diodes (LED) (Chen, C.H. *et al.*, 2009; Fang *et al.,* 2009), solar cells (Vomiero *et al.,* 2009; Xu *et al.*, 2009), nano-piezotronics and nano-generators (Wang, 2009a, Yang, R. 2009). These new developments and applications of semiconductor nanostructures have attracted both the scientific and industrial communities to focus on this class of materials. In semiconductor nanowires and nanobelts, the huge surface to volume ratio (~10^8 m^{-1} for nanowires as compared to ~10^2 m^{-1} for bulk materials) results in strong sensitivity of the excitons to surface states and as well as defects caused by their reduced size. Therefore, investigation on the electrical and optical properties in one-dimensional (1D) semiconductors is extremely important in order to understand in detail how the electronic states are modified by these types of effects in nearly 1D structure (e.g. NWs and NBs).

1.1 Background and scope of study

Semiconductors of interest include the semiconducting oxides, such as ZnO, SnO_2, NiO, MgO, and CdO. Of these, ZnO is particularly interesting for nanodevice applications. ZnO, as one of the most semiconducting materials, has a wide range of applications owing to its type of structure, electronic distribution and polarity (Yang, R.S *et al.,* 2009; Wang, Z.L. 2008). ZnO plays an important role in a wide range of applications reflected by the world usage of ZnO estimated at over a million tons in 2004, while European consumption was about 300,000 tones. A graph of ZnO usage in different zones of the world is shown in Fig. 1.1.

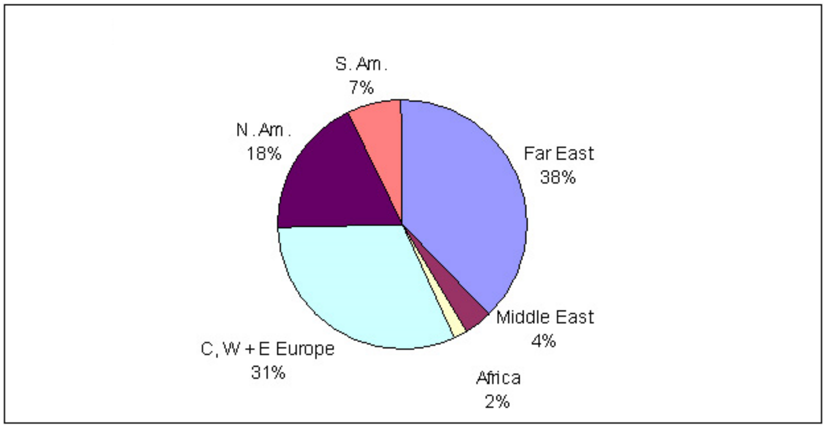

Figure. 1.1. Worldwide ZnO consumption per continent. (http://www.zincoxide.umicore.com/Applications/).

In addition, ZnO has shown splendid and abundant nanostructure configurations that a material can form. ZnO has a direct band-gap of 3.37 eV and a high exciton binding energy of 60 meV, which is greater than the thermal energy at room temperature. This semiconductor has important applications in electronics, optics, opto-electronics, lasers and LEDs (Jagadish *et al.,* 2006). The pyroelectric and piezoelectric properties of ZnO make it a good candidate for transducers, sensors, and energy generators, as well as in photocatalysis for hydrogen production (Yang, R.S *et al.,* 2009; Wang, Z.L. 2008). Furthermore, ZnO nanostructures have proven to be promising candidates for future cold electron sources. To date, field emission (FE) study has also been carried out on ZnO nanostructures (Shen *et al.*, 2006). With regard to their potential applications, an important challenge for FE is reducing the turn-on and threshold electric fields (Xiao *et al.*, 2008). In addition, ZnO is a green material that is bio-compatible, biodegradable, and bio-safety for medical and environmental applications (Zhou *et al.*, 2006; Li, Z *et al.*, 2009). Some optoelectronic applications of

ZnO overlap with that of GaN, another wide band-gap semiconductor (3.4 eV), which is widely used for the production of green, blue-ultraviolet, and white light-emitting devices (Ponce & Bour, 1997). However, compared to GaN, ZnO has two advantages: (i) ZnO has a larger exciton binding energy at room temperature (60 meV) than that of GaN (20 meV) (Liu *et al.*, 2004); and (ii) the crystal-growth technology associated with ZnO is much simpler than for GaN.

In fact, research on ZnO has been carried out since the 1930's in the form of thin films (Bunn, 1935); thus, ZnO is not a new material. Interest in ZnO research waned during the 1980's. However, interest on ZnO was renewed with the discovery of nanobelts (NBs) by Wang's group (Pan *et al.*, 2001) and the demonstration of ultra violet (UV) lasers in aligned nanowires (NWs) arrays (Huang *et al.*, 2001). Ever since, the number of papers published on ZnO nanostructures has increases exponentially (Fig. 1.2).

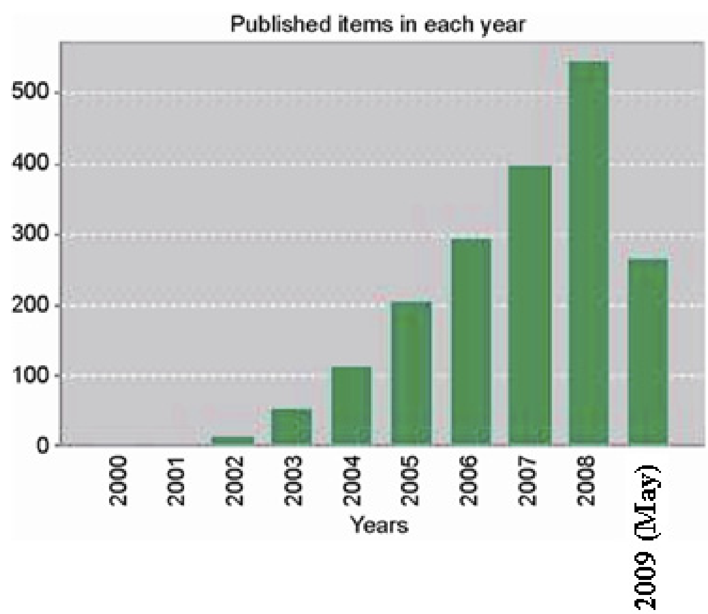

Figure 1.2. Publication statistics on nanostructures for ZnO. The data were received on May 20, 2009 through the Institute of Scientific Information (ISI) database using the following key words that appear in the title, abstracts, and keywords: ZnO (or zinc oxide) together with nanowire, nanobelt, nanorod, nanoribbon, nanotip, nanofiber, nanoring, nanohelix, nanospring, nanobrush, or nanoflower (Wang, 2009 b).

As shown in Fig. 1.2, over 550 papers were published on ZnO nanostructures in 2008. As for 1D nanostructures, ZnO is equally as important as Si-based 1D nanostructures, according to the literature, and it is playing an increasingly key role in the developing fields of nano-science and nanotechnology.

Figure 1.3 shows some important physical properties and applications of ZnO. Overall, carbon nanotubes, silicon NWs, and 1D ZnO structures have probably been the most important 1D nanomaterials in nanotechnology research during the past decade.

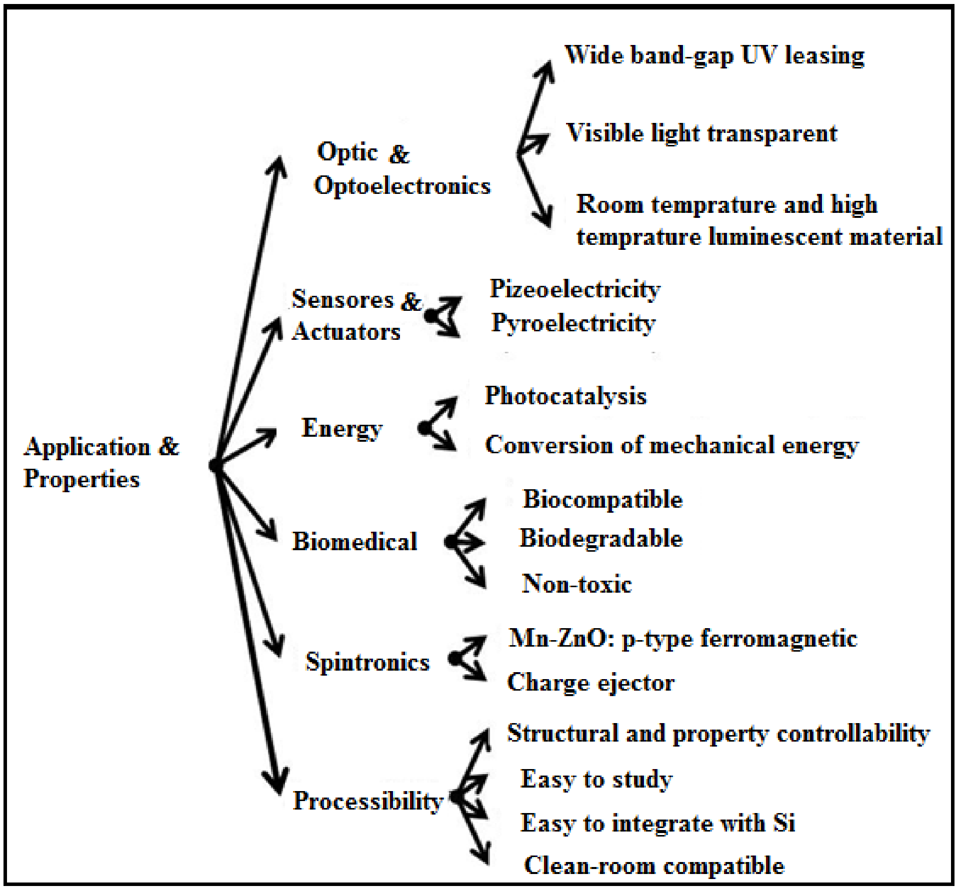

Figure 1.3. A summary of ZnO applications and properties (reformed from Wang, 2009a).

According to a 2008 report on the map of physics by *Physics World*, research into ZnO NWs is as important as that into dark matters, quantum computing, string theory, semiconductor thin films, photonic crystals, and carbon nanotube (Fig. 1.4) (Physics world, 2008).

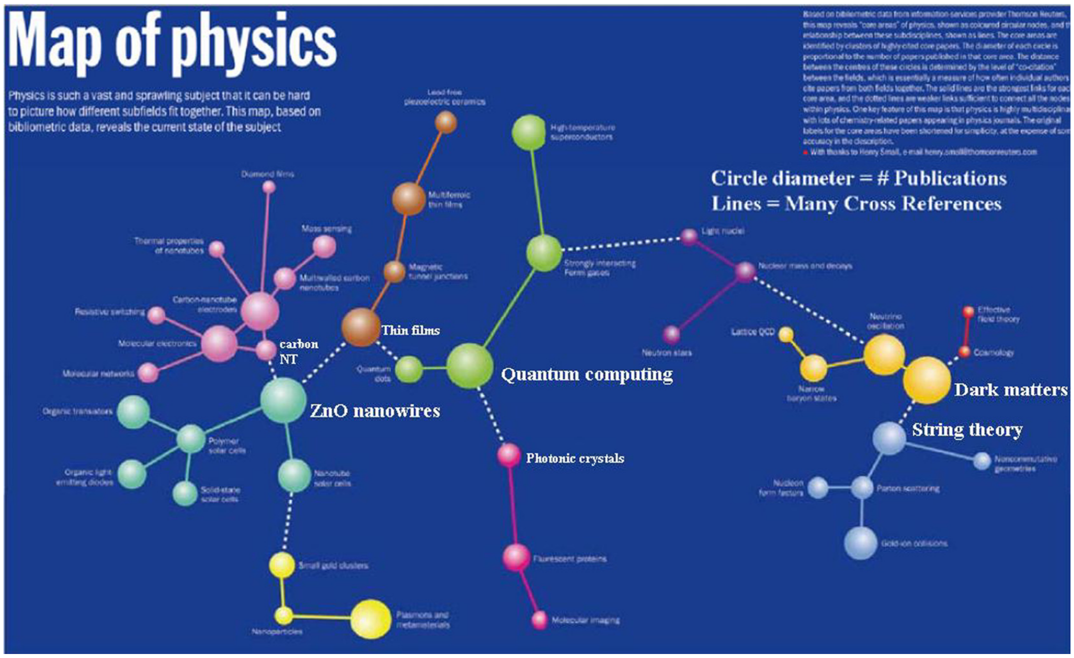

Figure 1.4 Showing the role of ZnO nanostructures. (from *Physics World,* October issue, 2008)

1.2 Aim and objectives

Optical and field emission properties of ZnO nanostructures are very important properties of ZnO due to several applications of these nanostructures in optoelectronic devices. Obtaining high quality nanostructures using inexpensive methods and doping materials is one of the biggest challenges in nanomaterials researches. It is known, thermal evaporation method is one of the inexpensive methods to growth of ZnO nanostructures. In addition, Mg, Al, In, Sn, and S are very common elements as dopants ZnO that some their effects on the properties of ZnO nanostructures are still unknown. Based on these observations, simple, inexpensive, but effective growth methods of ZnO nanostructures and its characteristics are presented in this thesis.

In particular the objectives in this thesis are:

i) To modify the thermal evaporation technique for producing undoped ZnO nanowires with improved optical properties.

ii) To investigate of size effects on the optical properties of undoped ZnO nanowires.

iii) To identify doping technique of ZnO nanostructures, such as:

Modification of thermal evaporation set-up and gold metal effects on Mg doping in ZnO nanowires including investigation of field emission of $Zn_xMg_{1-x}O$ nanowires;

Using AlN ultra thin film as a source for Al-doped ZnO nanowires;

Fabrication of ZnO/ZnInO heterostructure nanowires;

Comparative studies between optical properties of S as an anion and Sn as a cation dopant in ZnO nanobelts.

We expect a good quality undoped and doped ZnO nanostructures can be produced from the modified thermal evaporation technique, which will also allow detailed analysis of the previously unknown optical properties of ZnO nanostructures.

1.3 Thesis structure

Chapter One of this thesis introduces the general properties of ZnO and the importance of ZnO as a semiconductor. Chapter Two includes a literature review of 1D ZnO; fundamental properties of ZnO, and doping effects on optical properties of ZnO. Chapter Three deals with the experimental technique including thermal evaporation, vapor-liquid-solid (VLS), and vapor-solid (VS) methods for the growth of 1D ZnO structures, as well as characterization techniques used in this work. Chapter Four highlights the growth techniques of undoped ZnO nanowires in the conventional and modified thermal evaporation set-up. Further, the structures and optical properties of ZnO nanowires is discussed. Chapter Five presents the results of ZnO nanowires that were doped with Mg, Al, and In elements, and also their effects on optical properties of doped ZnO nanowires. In addition, for a specific case of Mg-doped ZnO nanowires, field emission characterization of nanowires is presented in this chapter. Chapter Six discusses a comparative study of optical properties between undoped, sulfur- and tin-doped ZnO nanobelts. Chapter Seven provides the conclusion this thesis as well as provide several suggestions for future works.