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SYNTHESIS OF ZINC OXIDE NANOSTRUCTURES BY
WET OXIDATION PROCESS

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A thesis submitted in partial fulfillment of
the requirements for the degree of Doctor of Philosophy
in Chemical and Materials Engineering
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The studies on zinc oxide (ZnO) nanostructures have been intensified worldwide in the last decade. This is because ZnO as a semiconductor material has some unique properties, such as a wideband gap of 3.37 eV and high exciton energy of 60 meV at room temperature. This makes ZnO a potential and low cost substitute for GaN for blue to ultra-violet (UV) light emitting applications. Furthermore, it is known that ZnO material can easily form various nanostructures such as nanowires and nanobelt, which have the potential for catalysis or solar cell applications due to their high specific surface area and reactivity. Up to now, a large range of ZnO novel nanostructures has been synthesized by different groups with different methods. However, most of the current used techniques either has problems regarding to the requirements for high temperature and/or vacuum conditions incorporating the necessity of using expensive equipments, or difficulties with quality control and pollution.

The focus of this thesis research is on the development of an alternative way of producing high quality ZnO nanostructures at moderate temperatures with low requirements in regard to facilities and experimental conditions. The method is wet oxidation, where Zn precursor is prepared by magnetron sputtering and oxidation of the Zn precursor films in wet O₂ to produce ZnO nanostructures. In this thesis, various experimental factors were studied for their impacts on the formation of ZnO nanostructures. The growth mechanism of the ZnO nanostructures was then derived and checked with the experimental results. The structural and optical properties of the ZnO nanostructures were characterized by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy
Abstract

TEM, cathodoluminescence (CL) and photoluminescence (PL) measurements to gain the understanding of the growth process in wet oxidation.

The doping methods for the wet-oxidation technique have been developed in two ways. Ag doping was achieved by mixing small amount of Ag into Zn precursor in advance of wet oxidation; and during the wet oxidation, the Ag atom would diffuse into the ZnO nanostructures to form Ag doping. Ag doping was confirmed by SEM, TEM, X-ray photoelectron spectroscopy (XPS) and PL. However, TEM observation showed that Ag doping was non-uniform in the ZnO nanowires, with a concentration gradient along the nanowire growth direction. XPS results demonstrated that the doped Ag existed in 1+ and 2+ chemical states, rather than in the metallic element state. PL spectra indicated that Ag doped ZnO nanowires had better light emission than the un-doped ZnO.

N doping was conducted by introducing NH\textsubscript{3} into the wet oxidation atmosphere, so that Zn could react with NH\textsubscript{3} at the same time as being oxidized. SEM studies demonstrated that the nanowires grew better from Ag-Zn precursor films than from Zn precursor films with the same oxidation conditions. The presence of Ag reduced the temperature required for the Zn-NH\textsubscript{3} reaction to take place. This resulted in the amount of Zn\textsubscript{2}N\textsubscript{3} crystals being so large that it could be observed under TEM. The Zn\textsubscript{2}N\textsubscript{3} crystals would transform to ZnO during the oxidation process with certain amount of N atoms remaining in the crystal lattice: this was confirmed by XPS measurement.

Wet oxidation can also be used to produce ZnO and ZnO/TiO\textsubscript{2} porous films. The porous structure was formed by reactive sputtering and preserved during wet oxidation. TiO\textsubscript{2} nano-clusters in anatase phase were formed on the surface of the ZnO/TiO\textsubscript{2} porous film after the wet oxidation, and the porous ZnO/TiO\textsubscript{2} film
showed enhanced PL spectrum in visible light range. The enhanced PL emission is believed to come from TiO₂ due to its resonant effect with ZnO.

Due to the large surface area resulted from the high porosity, ZnO and ZnO/TiO₂ films have shown great photocatalysis activity for degradation of organic compounds. The ZnO/TiO₂ porous film showed a better performance under visible light than the ZnO porous film, and more than 70% of the estrone could be degraded within 4 hr under visible light irradiation, with ZnO/TiO₂ porous film as the catalyst. A further increase of TiO₂ content in the porous film using the sol-gel method can increase the degradation percentage to more than 80% within the same time period. These tests demonstrated that these porous films would have great potential in the photocatalysis application.

Some directions of future development for this research are suggested in the last part of this thesis.
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CHAPTER 1. INTRODUCTION

1.1 ZnO: History and Future Development

Zinc oxide, with the formula ZnO, is an inorganic compound which presents in the earth’s crust as the mineral zincite [1]. It is not a novel material for scientific study, and has been widely used in industry. ZnO can be found in numerous materials and products as an additive including plastics, ceramics, glass, cement, rubber, paint, adhesives, sealants and pigments [2]. In these traditional applications, ZnO is valued for its ultra-violet (UV) absorbance, piezoelectricity and luminescence at high temperatures. It is even added to food such cereals as the source of Zn nutrient.

As a semiconducting material, ZnO was first studied as early as 1930s [3], and research focused on bulk ZnO growth, characterizations and applications had rapidly grown since then. By the end of the twentieth century, ZnO had been widely used in semiconductor industry as varistors operated at elevated temperatures or high voltages [4], and as ultrasonic transducers in high-frequency regions [5]. These kinds of applications of ZnO semiconductor were mainly based on its large electro-mechanical coupling factor, low dielectric constant and high stability at elevated temperature as a piezoelectric material.

From the mid 1990s, ZnO was again under the scientific spotlight. At that time, the initial reason that researchers started to pay attention to this material, was to develop high quality, closely lattice matched substrate materials for GaN which had been viewed as a promising wide band-gap material for short wavelength photonic applications, such as UV and blue light emitting diode (LED) and lasers [6]. However, along with the deeper research, it was found that ZnO itself is an excellent wide band-gap material, and can produce bright blue to UV light and laser [7-9],
which opened a new era for ZnO material. Since then numerous efforts have been devoted worldwide into the research for the realization of ZnO based photonic and optoelectronic devices. It is believed by many researchers that ZnO is a more prospective candidate for the next generation of light emitters for solid state lighting applications than GaN, even though the GaN-based LEDs have been commercialised and currently dominated the light emission applications in UV/blue wavelength range. This is because ZnO has several advantages compared to GaN. The two outstanding factors are [7, 9]:

1. The exciton binding energy of \(~60\text{meV} at room temperature\) is much higher than that of GaN (\(~25\text{meV}\)), which can enhance the luminescence efficiency of ZnO based light emission devices at room temperature, and lower the threshold for lasing by optical pumping.

2. The growth of high quality single crystal substrates is easier with lower cost than GaN.

As the research on ZnO went deep, increasingly interesting properties and potential applications have been discovered for this material. One of the most attractive aspects is that it is relatively simple for ZnO to form various nanostructures including highly ordered nanowire arrays, tower-like structures, nanorods, nanobelts, nanosprings and nanorings [10]. Due to the special physical and chemical properties derived from the nanostructures, ZnO has been found to be promising in many other applications, such as for sensing [11-13], catalysis [14-16], photovoltaics [17] and nano-generators [18, 19], just to name a few.

Despite the maturity of the field of semiconductors and the wide information base available for ZnO, there are a number of problems and hurdles to the scientific community, which need to be understood and overcome before ZnO based electronic devices, can be commercially realized.
Chapter 1. Introduction

One of the most important hurdles for the application of ZnO based devices is the stable and reproducible doping method for \( p \)-type ZnO film and bulk material [1]. ZnO is intrinsically an \( n \)-type semiconductor although discussions about the origins of the native donors have lasted a long time without reaching a consistent solution. The \( n \)-type doping of ZnO is relatively easy to produce. Group III elements Al, Ga and In are great donor dopants for ZnO, and each can produce carrier concentration in the range of \( >10^{20} \text{ cm}^{-3} \) [20, 21]. This kind of \( n \)-type ZnO film with good conductivity also shows excellent transparency, which is also promising for its application as transparent conductive oxide (TCO) films.

However, the \( p \)-type doping of ZnO with high quality and good reliability has, for many years, proved an enduring challenge. Although reports of \( p \)-type ZnO and homogeneous ZnO \( p-n \) junction are emerging all the time, their reliability and reproducibility is questionable. Most difficulties encountered are likely to be due to stability issues. It is obvious that the production of stable \( p \)-type ZnO is the critical point to be overcome if ZnO based device are ever to become a viable reality.

Compared to the production of \( p \)-type bulk ZnO or ZnO film, the effective and controllable \( p \)-type doping for ZnO nanostructures is even more difficult to realize. Vapour depositions or chemical solution methods are the most commonly used methods for the production of ZnO nanostructures, but in these processes, the dopant atoms are not easily incorporated into the crystal lattice of ZnO nanostructures due to the lowest energy and chemical equilibrium principles [22-24]. Ion-implantation is regarded as an effective method for ZnO nanostructure doping due to its non-equilibrium nature, however the energetic ions would reduce the quality of the crystal and induce large amount of defects [25].

Obviously, effective doping methods for ZnO nanostructures and the synthesis of ZnO nanowires with a \( p-n \) junction are still a challenge for the ZnO nano-devices.
Chapter 1. Introduction

The development of other synthesis techniques may enable this problem to be solved. The synthesis processes of ZnO nanostructures also need to be studied for improvement in the aspects of energy efficiency (for vapour approach), cost effectiveness (for processes such as Molecular Beam Epitaxy), and doping control (for solution methods), all of which have led to the motivation for, and objectives of, this thesis research.

1.2 Objectives

1. Growth of Zinc oxide nanowires by wet oxidation method

   The first objective of this study is to fabricate ZnO nanowires by using the wet oxidation method, and to investigate the influences of different experimental parameters on the formation of ZnO nanostructures, including the quality of Zn precursor, oxidation time, oxidation temperature, and humidity in the reaction chamber. This study should enable the ZnO nanostructure growth mechanisms in wet oxidation to be defined.

2. Development of Doping Method for Wet Oxidation

   The second objective is to find the way to achieve effective doping for ZnO nanostructure grown from wet oxidation, especially $p$-type doping. This study is necessary because that the current widely used method still cannot produce high-quality and stable $p$-type ZnO nanostructures. Wet oxidation may have an opportunity to contribute this.

3. Synthesis ZnO Based Porous Film

   Different ZnO structures, such as porous ZnO films, can be produced with wet oxidation method by altering the experimental parameters. ZnO and ZnO/TiO$_2$ composite porous films have great application potential in the areas of photocatalysis. A systematical study on their formation conditions in wet oxidation would further explores the application areas of wet oxidation process.
4. **Structure and Property Characterizations**

Microstructure and property characterizations are carried out to study the correlation of processing, microstructures and properties of ZnO materials, to determine the feasibility of the designed doping methods. The information obtained from property characterization can give indications for the potential applications for the materials produced by wet oxidation.

5. **Applications**

Based on the information obtained from the above four stages, prototype application tests are carried on the area of photocatalysis applications by using the ZnO nanostructures and porous films.

**1.3 Thesis Outline**

The thesis is structured as follows:

Chapter 2 gives an overview of some basic properties of ZnO, including the crystal structure, electronic and optical characters, as well as the current research progress or status of ZnO material. The typical synthesis and doping methods of both ZnO films and nanostructures are also introduced. The advantages and limitations of those methods are briefly discussed. Following these processing methods there is a description of the basic principles of the wet oxidation technique, which is discussed in more detail. Finally, some potential applications of ZnO are presented.

Chapter 3 describes the general experimental procedures that were used in this study, including the nanostructure synthesis processes, which consist of magnetron sputtering and wet oxidation; material physical and chemical analysis methods to comprehend the properties of the synthesized ZnO nanostructures.

Chapters 4 - 7 show the results from my own research work. These chapters are each structured to provide an introduction to the topic, including a complementary
Chapter 1. Introduction

literature review on the field to place the work into context, followed by specific experimental details, results, analysis, discussions and conclusions.

Chapter 4 deals with the setup of the wet oxidation method. The influences of various experimental parameters on the resulting ZnO nanostructure properties are systematically explored, and the optimum conditions for ZnO nanowires growth have been obtained. The growth mechanisms of ZnO nanowire are also studied based on the experimental results.

Chapter 5 develops the method to produce Ag doped ZnO (Ag:ZnO) nanowires based on wet-oxidation technique. The investigation on the Ag chemical state in the ZnO lattice and the optical properties of Ag:ZnO nanowires are emphasized.

The doping method for the wet oxidation technique is further explored in Chapter 6, in order to grow N doped ZnO (N:ZnO) nanowires. The properties of N:ZnO and N-Ag co-doped ZnO nanowire are studied. It is interesting to find that Ag seems to be able to enhance N doping, which is important for the realization of stable $p$-type ZnO nanostructures.

Chapter 7 explores the method to produce ZnO and ZnO/TiO$_2$ porous films. The effects of experiment parameters are investigated and the film properties are examined. The catalysis performance of the ZnO/TiO$_2$ nano-porous films is tested by degrading estrone under UV and visible light irradiation. Estrone is a pollutant that comes from dairy farms, and is particularly relevant to the environment protection and economy of New Zealand and Australia.

Finally, in Chapter 8, the conclusions for the entire thesis are drawn and possible future directions are suggested for the research on ZnO materials.
CHAPTER 2. LITERATURE REVIEW

In this chapter, an overview of the basic properties of ZnO, including the crystal structure, electronic and optical characteristics is delivered. The commonly used techniques for ZnO film and nanostructure synthesis and doping are also introduced. Finally, some current and potential applications of ZnO are presented.

1.1 ZnO Properties

2.1.1 Crystal Structure

Theoretically, ZnO can have 4 crystal structures: cubic zincblende, rocksalt, cubic caesium chloride, and wurtzite (B4 type) structure. Among them, wurtzite structure is the most common ZnO phase at ambient pressure and temperature. Zincblende ZnO is stable only by growth on cubic structures [27-29]. Rocksalt structure is a high-pressure metastable phase forming at ~10 GPa, and can not be epitaxially stabilized [30]. Cubic caesium chloride ZnO is only indicated possibly existing at extremely high temperature by theoretical calculation [31]. Figure 2-1 shows the crystal structures of rock salt and zincblende phases of ZnO.
Figure 2-2. The crystal structure of wurtzite ZnO in 3-D representation, a) with bonding shown, and b) with typical planes shown.

ZnO wurtzite structure is a hexagonal lattice, belonging to the space group P63mc, as if two sub-lattices of HCP Zn$^{2+}$ and HCP O$^{2-}$ interconnected, such that Zn ions are surrounded by a tetrahedral of O ions, and vice-versa (Figure 2-2). The lattice parameters are $a = 0.32495$ nm and $c = 0.52069$ nm [2]. Experimentally, for wurtzite ZnO, the real values of $c/a$ and $u$ were determined in the range of 1.593-1.6035 and 0.3817-0.3856, respectively [32]. Zn-O bond possesses a strong ionic character. However, tetrahedral coordination also commonly indicates the sp$^3$ covalent bonding, and thus ZnO lies on the borderline between being classified as a covalent and ionic compound [26]. A number of properties of ZnO are resulted from this tetrahedral coordination, such as its piezoelectricity and spontaneous polarization, since a polar symmetry along the hexagonal axis is risen from the coordination. This coordination is also a key factor for ZnO crystal growth, etching and defect generation.

There are four most common face terminations of wurtzite ZnO: the polar Zn terminated (0001) and O terminated (0001$^-$) faces (c-axis oriented), the non-polar
(11 \overline{2} 0) (a-axis) and (10 \overline{1} 0) faces which both contain an equal number of Zn and O atoms. The polar faces are known to have different chemical and physical properties. The (0001) plane is basal, and the O-terminated face possesses a slightly different electronic structure to the other three faces [33]. Additionally, the polar faces and the (10 \overline{1} 0) surface are found to be stable, while the (11 \overline{2} 0) face is less stable and commonly has a higher surface roughness. These characters play an important role in the growth process of ZnO nano-structures.

2.1.2 ZnO Basic Physical and Chemical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Formula</td>
<td>ZnO</td>
</tr>
<tr>
<td>Molecular Weight:</td>
<td>81.37</td>
</tr>
<tr>
<td>Appearance:</td>
<td>white or yellow-white</td>
</tr>
<tr>
<td>Odour:</td>
<td>Odourless</td>
</tr>
<tr>
<td>Crystal System at 300K</td>
<td>Wurtziite</td>
</tr>
<tr>
<td>Space Group</td>
<td>P6,mc</td>
</tr>
<tr>
<td>Lattice constant</td>
<td>a = 0.32495 nm, c = 0.52069 nm</td>
</tr>
<tr>
<td>Sublimation point</td>
<td>1975 ± 25°C</td>
</tr>
<tr>
<td>Solubility</td>
<td>0.16 mg/100 mL (30 °C)</td>
</tr>
<tr>
<td>Hardness</td>
<td>4 moh</td>
</tr>
<tr>
<td>Dielectric constants</td>
<td>$\varepsilon_{11} = 8.55$, $\varepsilon_{33} = 10.20 \times 10^{-11} \text{ F/m}$</td>
</tr>
<tr>
<td>Density</td>
<td>$5.665 \times 10^3 \text{ kg/m}^3$</td>
</tr>
<tr>
<td>Thermal expansion coefficient</td>
<td>$\alpha_{11} = 4.0$, $\alpha_{33} = 2.1 \times 10^{-6/\degree C}$</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.6, 1-1.2</td>
</tr>
<tr>
<td>Energy gap</td>
<td>3.37 eV</td>
</tr>
<tr>
<td>Intrinsic carrier concentration</td>
<td>$&lt; 10 /\text{cm}$</td>
</tr>
<tr>
<td>Exciton binding energy(at room temperature)</td>
<td>60 mV</td>
</tr>
<tr>
<td>Electron effective mass</td>
<td>0.24</td>
</tr>
<tr>
<td>Electron Hall mobility at 300 K for low n-type conductivity</td>
<td>200 cm$^2$/V⋅s</td>
</tr>
<tr>
<td>Hole effective mass</td>
<td>0.59</td>
</tr>
<tr>
<td>Hole Hall mobility at 300 K for low p-type conductivity</td>
<td>5.50 cm$^2$/V⋅s</td>
</tr>
<tr>
<td>Optical transparency</td>
<td>0.4-2.5 (\mu) m</td>
</tr>
<tr>
<td>Refractive index</td>
<td>$n_p=1.9985, n_e=2.0147 (\lambda=6328 \AA)$</td>
</tr>
<tr>
<td>Electro-optic constant</td>
<td>$r_{33}=2.6$, $r_{33}=1.4 (\times 10^{-12} \text{ m/V}, \lambda=6328 \AA)$</td>
</tr>
</tbody>
</table>
Wurtzite ZnO is white or yellowish powder in its bulk form, nearly insoluble in water. It has a molecular weight of 81.37, average atomic weight of 40.69 amu, density of 5.665 g/cm and enthalpy of formation of -350.5 kJ/mol at 298.15K. The basic physical and chemical and properties of ZnO are presented in Table 2-1.

2.1.3 Energy Band Structure

![Figure 2-3. The LDA band structure of bulk wurtzite ZnO calculated using dominant atomic SIC-PP [34].](image)

A number of groups have calculated the electronic band of ZnO [31, 34-39]. The standard local density approximation (LDA) tends to underestimate the band gap by ~3 eV due to its failure in accurately modelling the Zn 3d electrons. However, by incorporating atomic self-interaction corrected pseudopotentials (SIC-PP), the Zn 3d electrons can be accurately accounted. The calculation is shown in Figure 2-3 [34]. The band structure is shown along high symmetry lines in the hexagonal Brillouin...
zone. Both the valence band maxima and the lowest conduction band minima occur at the $\Gamma$ point $k = 0$ indicating that ZnO is a direct band gap semiconductor. The band gap as determined from this calculation is 3.77 eV [34], which correlates reasonably well with the experimental value of 3.4 eV, and is much closer than the value obtained from the standard LDA calculation. Advantages associated with its large band gap include high breakdown voltages, ability to sustain large electric fields, low noise enervation, and high-temperature and high-power operation [40].

Figure 2-4. Schematic diagram representing the crystal-field and spin-orbit splitting of the valence band of ZnO into 3 sub-band states A, B and C at 4.2K [41].

The electronic structure of the surface of wurtzite ZnO was also extensively studied. Ivanov and Pollmann used the empirical tight-binding method (ETBM) to determine a Hamiltonian of the bulk states: the scattering theoretical method was applied to determine the nature of the surface states [42]. The calculated data was found to be in very good agreement with experimental results obtained from electron-energy-loss spectroscopy (EELS) and ultra-violet photoelectron
spectroscopy (UPS). It suggests that the Zn face possesses more covalent character, arising from the Zn 4s-O 2p states, whilst the O face is more ionic.

Experimentally, the ZnO valence band is split into three band states, A, B and C by spin-orbit and crystal-field splitting. Figure 2-4 schematically illustrates this splitting. The A and C sub-bands are known to posses $\Gamma_7$ symmetry, and the middle band B, has the $\Gamma_9$ symmetry [41]. The band gap has temperature dependence up to 300 K given by the relationship:

$$E_g (T) = E_g (T = 0) + \frac{5.05 \times 10^{-4} T^2}{900 - T}$$

These properties, combined with the lattice dynamic of ZnO give rise to interesting optical properties which will be discussed in Section 2.1.6.

### 2.1.4 Lattice Dynamics

**Table 2-2. Experimentally determined principal phonon modes of wurtzite ZnO at 300K [41]**

<table>
<thead>
<tr>
<th>Phonon mode</th>
<th>Value(cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_2^\text{low}$</td>
<td>101</td>
</tr>
<tr>
<td>$E_2^\text{high}$</td>
<td>437</td>
</tr>
<tr>
<td>TO($A_1$)</td>
<td>380</td>
</tr>
<tr>
<td>LO($A_1$)</td>
<td>574</td>
</tr>
<tr>
<td>TO($E_1$)</td>
<td>591</td>
</tr>
</tbody>
</table>

In single crystal wurtzite ZnO, there are 4 atoms per unit cell, giving rise to 12 phonon modes as follows: 1 longitudinal-acoustic (LA), 2 transverse-acoustic (TA), three longitudinal-optical (LO) and 6 transverse-optical (TO) branches. The $A_1$ and $E_1$ branches are Raman and infrared active, while the 2 $E_2$ branches (non-polar) are only Raman active. The $E_2^\text{low}$ mode is associated with vibration of the Zn sub-lattice, and the $E_2^\text{high}$ mode is associated with the oxygen atoms only. The $B_1$ branch is
always inactive. These modes are important for understanding the thermal electrical and optical properties of the crystal. Peaks resulted form these phonon mode can often be detected in low temperature photoluminescence (PL) measurement, and have been used to help assigning designations to other PL peaks [43, 44]. The phonon modes of ZnO have been extensively studied and modelled [40]. Table 2-2 gives a list of experimental values for the most common phonon modes visible at 300K [41].

2.1.5 Electrical Properties

The electrical properties of ZnO are hard to quantify due to large variance of the quality of samples available. The background carrier concentration varies a lot according to the quality of the layers but is usually at the level of $10^{16}$/cm$^3$. The largest reported n-type doping is $\sim 10^{20}$ electrons/cm$^3$ and the largest reported p-type doping is $\sim 10^{19}$ holes/cm$^3$. However such high levels of p-conductivity are questionable and have not been experimentally verified [45]. The exciton binding energy is 60 meV at 300K, and is one of the reasons why ZnO is so attractive for optoelectronic device applications at room temperature. The electron effective mass is 0.24 $m_0$, and the hole effective mass is 0.59 $m_0$. The corresponding electron Hall mobility at 300K for a low n-type conductivity is $\mu = 200$ cm$^2$/V•s, and for a low p-type conductivity is 5-50 cm$^2$/V•s [46]. The relatively high electron mobility makes ZnO hold advantages over other wide-band gap materials such as TiO$_2$ on the photo-electro-chemical applications, including dye sensitized solar cell (DSSC) and photocatalysis.

As-grown ZnO has always been found to be n-type. It was always assumed that the dominant donor was either O vacancy V$_0$, or the Zn interstitial Zn$_i$, since most sample are grown under Zn-rich conditions. However, this conclusion was
challenged by Kohan et al [47] and Van de Walle [48] in 2000 from different aspects. Kohan showed that both $\text{VO}$ and $\text{ZnI}$ theoretically had high formation energies in $n$-type ZnO, and therefore neither $\text{VO}$ nor $\text{ZnI}$ would exist in measurable quantities. Furthermore, it was also indicated that $\text{VO}$ and $\text{ZnI}$ were deep donors, so even if one or other were present, its ionization energy would be too high to produce free electrons. Although other theoretical analysis suggested that $\text{ZnI}$ was actually a shallow donor [49, 50], and had been proven by electron-irradiation experiments [8], the high formation energy of $\text{ZnI}$ mentioned earlier still limited its ability to contribute to $n$-type conductivity.

Meanwhile, Van de Walle’s results suggested that hydrogen (H) was likely to be a dominant background donor in ZnO materials which were exposed to H during growth, as H is easily ionized with a low enough formation energy to be abundant, and always a donor in ZnO. This proposal has been tested using ZnO prepared by seeded chemical vapour transport (SCVT) technique, and the results have confirmed that a shallow donor due to H exists in SCVT ZnO, and can contribute significantly to its conductivity [51-53].

The fact and evidence mentioned above led to the opinion that native donors, $\text{VO}$ and $\text{ZnI}$, do not play a significantly role in the conductivity of as-grown ZnO. However, Look’s work also suggested that $\text{ZnI}$ did contribute significantly to conduction in ZnO, but as complexes, probably $\text{ZnI-NO}$, instead of isolated elements [54].

Most ZnO nanostructures are single crystalline, possessing of superior electrical properties than polycrystalline ZnO thin films, but is not easy to be accurately determined. Several techniques have been developed to address this topic, including assembling field effect transistors (FET) with individual ZnO nanowire [55-59] and using conductive atomic force microscopy (AFM) [57]. These studies demonstrated
that the ZnO nanowires grown by chemical vapour deposition (CVD) exhibited an electron field-effect mobility of as high as 80 cm²/V·s [59]. In contrast, 7 cm²/V·s was already regarded quite high for ZnO thin film transistors [60]. If eliminated the effect of surface states on the electron transport, electron mobility of 1000 cm²/V·s can be achieved [59], which is much higher than the reported highest room temperature electron mobility of a bulk ZnO single crystal (205 cm²/V·s) [40].

Figure 2-5. a) Schematic of using an AFM probe to measure the individual ZnO nanowires. b) I-V curves obtained from a vertical nanowire using conductive AFM probes with Ti and Pt coating. c) I-V curves obtained from a vertical nanowire grown in an un-annealed anodic alumina membrane (AAM). d) I-V curves obtained using conductive AFM with and without UV illumination from a single nanowire grown in an annealed AAM [61].
Chapter 2. Literature Review

The high electron mobility of ZnO nanowire makes it very attractive to researchers in the field of DSSC development. It is regarded as one of the most feasible ways to improve the TiO₂ based DSSC development. However, there are still some problems need to be addressed for measuring the electrical properties at nanoscale. For example, Figure 2-5 illustrated how the nanowire electrical properties is measured by AFM probe, and the results shows with different AFM probe coating, the measurement gave different result due to the contact nature between the probe and the nanowire. Other issues such as property change due to deformation (as ZnO is piezoelectric material), insulating layer properties, variation in crystal quality between individual nanowires, may all result in inaccurate measurement.

2.1.6 Optical Properties

Table 2-3. Static ($\varepsilon_0$) and high frequency dielectric constant ($\varepsilon_\infty$) data for ZnO

<table>
<thead>
<tr>
<th></th>
<th>Film</th>
<th>Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_0$ E ⊥ c</td>
<td>7.46</td>
<td>7.77</td>
</tr>
<tr>
<td></td>
<td>E \parallel c</td>
<td>8.59</td>
</tr>
<tr>
<td>$\varepsilon_\infty$ E ⊥ c</td>
<td>3.70</td>
<td>3.60</td>
</tr>
<tr>
<td></td>
<td>E \parallel c</td>
<td>3.78</td>
</tr>
</tbody>
</table>

The fundamental optical properties of ZnO, such as refractive index and dielectric constants, have been determined by a number of comprehensive studies [62, 63]. The measurements were carried out using spectroscopic ellipsometry. The values determined for the dielectric constants of ZnO are shown in Table 2-3 [63], and the refractive index of wurtzite ZnO is commonly given as $m_ω = 2.008$ and $n_e = 2.029$ [64]. The work of Meyer et al gave a comprehensive treatment and analysis of the excitonic spectra obtained from bulk, n-type ZnO, and assigned many defect related spectral features, as well as donor-acceptor pair (DAP) emission [41].
Chapter 2. Literature Review

Figure 2-6 shows a typical photoluminescence spectrum of n-type ZnO measured at 4.2 K. The excitonic, DAP and extended green band emissions can all be clearly seen. The excitonic emissions are the intrinsic optical transitions that take place between the electrons in the conduction band and holes in the valence band. Excitons are classified into free and bound excitons. The DAP and extended green band emissions are the extrinsic features related to dopants and defects, which usually create discrete electronic states in the band gap, and therefore influence both optical-absorption and emission processes [40]. The extended green band emission is a broad defect related peak extending from ~1.9 to ~2.8 eV, and is also a common optical feature of ZnO. The origin of its luminescence is still not well understood, and has in the past been attributed to a variety of different impurities and defects [8, 65-69]. Among the different mechanisms proposed to explain the visible
luminescence, oxygen vacancies have been widely considered as the most probable candidate [43, 51, 53, 70, 71].

Figure 2-7 shows a comparison of PL spectra between un-doped and N doped ZnO film grown by molecular beam epitaxy (MBE) reported by D.C Look [43]. It demonstrates that the doping of N doping significantly changed the ZnO PL spectrum. Peak at 3.315 eV related to the acceptor site ($A^0_X$) is enhanced by the doping.

![Figure 2-7. PL spectra, at 2 K, for two ZnO samples, an un-doped bulk sample, and an N doped, MBE-grown epitaxial layer [43].](image)

2.1.7 Dopants for ZnO

Same as other semiconducting materials, properties of ZnO, including electrical, optical and magnetic characters can be substantially modified by various doping elements to the ZnO crystals. For example, by doing transition magnetic elements
such as Co, ZnO can exhibit spintronic behaviours [72-76], which is another research direction related to ZnO. As the main interest of ZnO is still concentrated on its electrical and optical properties, the dopant elements are introduced according to their effects on the electrical properties in the following sections.

2.1.7.1 Donor Dopants

Group III elements Al, Ga and In are good donor dopants for ZnO, and each can produce carrier concentration in the level of $> 10^{20} \text{cm}^{-3}$ [20, 21], and this type of ZnO produces some of the highest-conductivity for transparent materials available today.

Group VII elements F, Cl, Br and I also act as donor as they substitute O site. It has been reported that F doping can greatly increase the conductivity in ZnO films grown by chemical spray techniques [77, 78]. However, there is not much electrical or optical evidence supporting that they are significant background dopants, as the increase in $n$-type electrical conductivity is resulted from the extra free electrons from Zn atoms when bonded to Group VII elements.

2.1.7.2 Acceptor Dopants

Theoretically, Group I elements, Li and Na, should be good acceptor dopants for ZnO when they are on Zn sites, but it turns out that doping Li almost always produces semi-insulating (SI) material [43, 79]. This is due to that Li interstitial Li$_i$ has lower formation energy than Li$_{Zn}$ in $n$-type ZnO, and Li$_i$ is a donor. Thus, a sample with high Li concentration would have a problem of self-compensation, balance between Li$_{Zn}$ and Li$_i$, giving a Fermi level close to the mid gap, and produce SI materials. The same problem is also evidently held for Na.

Group V elements, N, P, As and Sb, are important for realization of $p$-type ZnO. N should be a good acceptor dopant, as its electronic core structure and ionic radius
are similar to those of O and ready to take O site. N concentration of \(10^{20}/\text{cm}^3\) having been measured in many N doping ZnO samples, primarily as acceptor on O site, but the real active acceptor concentration is in a much lower range (\(\sim10^{15}\) to \(\sim10^{17}/\text{cm}^3\)). This is because that most of the N atoms are passivated, mainly by H [64, 80-87].

Although it seems difficult to make good \(p\)-type ZnO through N doping, it is promising to produce good \(p\)-type materials by doping with other three Group V elements, P, As and Sb in different mechanism. By using density functional theory (DFT), Limpijumnong et al found that a complex, \(\text{As}_{\text{Zn}}\)-2\(\text{V}_{\text{Zn}}\), has a rather low formation energy to act as the acceptors in ZnO host [88]. Other studies also found that the implanted As tends to go on the Zn site [89], further confirmed Limpijumnong et al’s finding.

Transition metals that can give monovalent ions are also investigated for possibility of being acceptors for ZnO. For example, Ag is a potential candidate, if it can incorporate in substitutional Zn sites. With conventional wisdom, Ag doping should not have the problem of self-compensation as described above for Group I doping, since \(\text{Ag}^+\) has larger radius (0.122 nm) than host \(\text{Zn}^{2+}\). Therefore, it is less likely to go to interstitial sites, although it makes it harder to substitute \(\text{Zn}^{2+}\) too. However, Fan and Freer suggested that Ag may act as amphoteric dopant, existing both on substitutional Zn site and the interstitial site, in their report about Ag doped ZnO for application of varistors [90]. In addition, Kanai reported that Ag behaved as an acceptor with deep level \(\sim0.23\) eV below the conduction band [91].

Perhaps due to these reasons, there are not much recently studies on Ag doped ZnO, compared to other dopants, but there are some results indicating that Ag has the potential for \(p\)-type realization and optical applications of ZnO [44, 92-97]. As Ahn reported, there is a short temperature interval for pulsed laser deposition, \(200^\circ\text{C}\)
to 250°C, where Ag doped ZnO shows $p$-type conductivity, with the carrier concentration in the range of $10^{16}$–$10^{17}$ cm$^{-3}$ [92], and it was also reported Ag doping can enhance the UV emission of ZnO [93, 98].

Compared with the doping to ZnO film, the effective and controllable doping for ZnO nanostructures by vapour deposition or chemical solution methods was still far from practical application, since the dopants atoms were not easy to incorporate into the crystal lattice of ZnO nanostructures due to the minimum energy principle [22-24]. Ion-implantation was regarded as an effective method for ZnO nanostructure doping, whereas the energetic ions would reduce the quality of the crystal and induce large amount of defects [25].

### 2.2 Synthesis of ZnO Film and Nanostructures

A variety of methods has been used for synthesis ZnO film and nanostructures. For consolidation, methods have been categorized as either physical vapour deposition (PVD), CVD, or solution based chemistry (SBC), PVD and CVD fall into the category of gas-phase approach where high vacuum and/or elevated temperature are normally required. Each respective method can be sub-divided into the individual technique that will be introduced in the following sections.

#### 2.2.1 Physical Vapour Deposition (PVD)

PVD operates when a material is physically released from a source and transferred to a substrate. It describes the solidification of a vapour directly onto a surface such that no chemical reaction takes place. If a chemical reaction does occur with the vapour, and/or with the deposition surface, then the process is not PVD but rather CVD. The three most common and important PVD technologies for ZnO deposition are thermal evaporation, pulsed laser deposition (PLD), and sputtering, each of which will be introduced below.
2.2.1.1 Thermal Evaporation

The thermal evaporation basically follows the vapour-solid (V-S) mechanism. Usually ZnO powders are placed inside a vacuum chamber, where the vacuum condition is kept in the range of $10^{-2}$ to $10^{-9}$ Torr. The ZnO powder will be heated up by a heating source to its vapour point once the appropriate pressure within the vacuum chamber is reached. The vaporized ZnO will condense along the cooler surfaces in the vacuum chambers, as well as on the collection substrate. By varying the experimental temperature, pressure in the chamber, atmosphere and facility configuration ZnO thin films and various nanostructures can be produced by this method.

Electron beam, radio frequency (RF) inductive, and resistive heating are the heating sources typically used in thermal evaporation. Electron beam and RF inductive heating are used to create localized heating of the source material, which have been limited to produce highly oriented ZnO thin films [70, 99, 100]. Resistive heating is a non-localized heating source and commonly used for furnace applications. For example, a tube furnace with appropriate design and control can create a specific temperature gradient along the tube, which is useful for nanostructure production [101-104]. A variety of ZnO nanostructures like nanobelts, nanocages, nanospings, nanorings and nanohelix have been synthesized by Wang’s group using this method [10]. However, high energy is required to give elevated temperature (over 1000°C) and doping process can be achieved but difficult in this system.

2.2.1.2 Sputtering

Sputtering is the removal of surface atoms via high energy ions. The modern sputtering system uses a magnetron sputtering configuration, where a strong
magnetic field is applied to concentrate the plasma near the target to increase the
deposition rate. Certain level of vacuum is required for the sputtering system. When
applied to ZnO, residual pressure at the level of 10^{-6} Torr and working gas pressure
at the level of 10^{-3} Torr is enough to conduct the experiment. During the experiment,
after evacuation of foreign gas, an inert gas normally Ar as the working gas, is
introduced into the vacuum chamber where the source material target and substrates
have been placed in. Then a direct current (DC) or RF power supply is used to
ionize the inert gas so as to produce charged plasma. The ions are accelerated to the
surface of the target, and bombarding the atoms of the source material out of the
target. Resultantly, some of those atoms condense on the substrate to form films. A
bias voltage sometimes is applied to the substrate to assist the deposition, and
enhance the adhesion properties of the film to the substrate. The substrate can be
heated to improve the crystal quality of the growing film.

Normally DC sputtering is used for conductive target, but not suitable to
insulating materials due the build-up of positive charge on the target materials, while
an RF power can be used to solve this problem. ZnO is semiconductor, so it is
conductive enough to use both DC and RF sputtering. Sputtering is commonly used
to produce polycrystalline thin-film of ZnO at room temperature. RF sputtering can
produce ZnO film with better $n$-type conductivity, while almost insulating ZnO film
can be obtained by DC sputtering. Doping is possible to achieve with sputtering
system by the means of introducing gases containing dopant elements or mixing
dopant materials into the target. Our group had successfully produced high
conductive $n$-type ZnO film by Al doping with magnetron sputtering [105].
2.2.1.3 Pulsed Laser Deposition (PLD)

PLD is another popular technique for the synthesis of thin films and nanostructure materials. High vacuum condition is also required for this process. A laser beam is focused through vacuum onto the surface of a target material during the deposition. Sufficient high flux density and short pulse duration is requested to heat up the target rapidly to its evaporation temperature so as to form a vapour plume. The laser ablation produced vapour plume that has the similar stoichiometry of the target material, which is one of the major advantage of PLD [106]. Once the vapour plume has been formed, it is collected onto a cooler substrate that promotes nucleation and growth of crystalline films. The epitaxial single-crystalline ZnO film with quality as good as those from MBE can be produced by this method [107]. Doping can be conducted relatively easily through PLD by using targets with designed composition or a multi target system, and the doping level can be precisely controlled and monitored during the deposition [69, 108-110]. ZnO nanostructures such as aligned ZnO nanorods can also be synthesized by PLD [111]. The main practical limitation of PLD is its relatively low duty cycle and incorporation of particulates in the deposited films. Up scaling for industrial production and deposition of zinc oxide on large area substrates is still a major concern.

2.2.1.4 Glancing Angle Deposition (GLAD)

GLAD mainly developed by Brett’s group is a technique that can be achieved by using the traditional PVD method, such as sputtering, thermal evaporation and PLD to produce nanostructures [112-118]. Taking the sputtering as an example, its main principle is that the substrate tilted to have an angle to the target, and the substrate-target distance and the vacuum pressure are adjusted to that the substrate-target distance is smaller than that of the gas atom mean free path. This ensures that most
atoms coming out of the target do not clash to any of the gas atoms before reaching the substrate, so that all the atoms have the same incident angle with the substrate. In this case, soon after the deposition starts, the already deposited atoms will create shadows behind them, shielding the area from the other incident atoms. No further material deposition will occur in these regions, which can result isolated nanostructure arrays. Figure 2-8 illustrated the growth mechanism of GLAD, and nanowire array produced by GLAD [112]. ZnO nanostructure has also been produced by this technique [119].

Figure 2-8. The GLAD mechanism and nanostructures produced by GLAD [112].
2.2.2 Chemical Vapour Deposition (CVD)

CVD involves the chemical reaction between the vaporized source material and source gases, and/or with the deposition surface. The product of the reaction condenses during the formation of a solid material within the reaction vessel where the pressure and gas flow are controlled. The most common CVD techniques used to deposit ZnO are thermal CVD, low pressure CVD (LPCVD), plasma-enhanced CVD (PECVD), laser CVD (LCVD) metal-organic CVD (MOCVD), MBE, and atomic layer deposition (ALD), classified by the differences of the vacuum control level, heating source and reactants gas types etc.. For each of these methods, a vacuum chamber with gas flow control is required.

In CVD process both vapour-liquid-solid (V-L-S) and V-S growth mechanisms can occur. For V-L-S method, catalyst seeds are needed. During the reaction, the catalyst seeds are in liquid form, and the droplets serve as preferential sites for absorption of the gas phase reactant. The catalyst is selected so that the component elements of nanostructures are soluble in it, but do not form solid compound more stable than the desired nanostructured phase. Therefore, when the droplets become supersaturated, these nucleation sites start crystallization, and growth of nanostructures begins until the temperature drops below the eutectic temperature of the catalyst alloy or reactant is no longer available [120].

Au is commonly used as the catalyst to grow ZnO nanowires, but it is reported that Sn can also be the catalyst for growing ZnO nanorods [101]. The V-S mechanism is similar to that in PVD process. Parameters such as deposition temperature and pressure, oxygen partial pressure, carrier gas flux are important factors influencing the growth mechanism that governs the final structural features of ZnO nanostructures [104, 121]. ZnO nanowires, dendritic side-branched/comb-like structures, and nanosheets can be synthesized under the identical conditions
only with increased oxygen content [122]. Some of the specific CVD techniques are introduced below.

2.2.2.1 Thermal CVD & LPCVD

The experimental setup for thermal CVD is similar to the thermal evaporation. The required pressure level is $10^3$ Torr for the process. A solid source could be placed upstream. The solid is vaporized through heating, which is transported by a carrier gas that feeds the catalyst and source material for nanowire growth. LPCVD deposition is an old technique in industry for oxide film growth. In some research, it is the interchangeable term with the thermal CVD, but its working pressure range is slightly different. In LPCVD deposition process, the pressure is controlled to under 0.1 Torr. In the case of ZnO, both thermal CVD and LPCVD require lower operation temperature then thermal evaporation, but still over 900°C. Research has shown that they are feasible for production of various ZnO nanostructures [103, 121, 123].

2.2.2.2 PECVD & LCVD

In comparison with thermal CVD and LPCVD, PECVD are performed at much lower temperature, down to 300°C. The plasma is generated to compensate the low temperature, and increase the energy available to the chemical reaction. This technique is usually used for ZnO film preparation [124]. In LCVD, laser ablation with controlled doses is used as the heating source, which leads to precise dimension and doping controls for nanostructure. Super-lattices [125, 126] and core shell structures [126] can be produced by this method.

2.2.2.3 MOCVD

MOCVD is almost identical to the other types of CVD, only that metal-organic precursors are use to catalyze the chemical reaction. MOCVD needs to be carried
out at a very high level of vacuum and elevated temperature, and has been extensively used for synthesis of ZnO thin films and nanostructures. Doping is relatively easy to be conducted [84, 127-129]. However, metal-organic compounds are usually more expensive than inorganic compounds.

2.2.2.4 MBE

MBE is recognized as a technique for preparing high-quality layers, superlattices and hetero-structures with excellent thickness control, composition uniformity, and sharp dopant profiles. The term “beam” is used because the process takes place at ultra high vacuum chamber, and thus the mean-free-paths of the source materials vapours are sufficiently large to prevent all atomic interaction before arrive at the substrate. The vapours are from element sources with high purity which are slowly heated in individual quasi-knudsen cells, and released into the vacuum chamber by computer-controlled shutters. Upon condensation onto the single-crystal substrate, the elements from the vapours will start to interact with each other as well as with the substrates, and then atomic layers are epitaxially grown one layer at a time. The crystal quality and layer thickness can be monitored by reflective high energy electron diffraction (RHEED) during the crystal growth.

MBE method can produce very high quality single crystal ZnO film and nanostructures [43, 58, 59, 130]. However, the MBE system is very expensive and the operation conditions must be accurately monitored and controlled. It is therefore more suitable for scientific research in the laboratory scale.

2.2.3 Solution Based Chemistry (SBC)

Compared to vapour phase approaches, solution growth methods have the advantages of low growth temperature, potential for easy scaling up, and simplicity for fabrication of some nanostructures. Methods for the synthesis of ZnO
nanostructures in chemical solutions are commonly conducted at relative low temperatures (60-300°C). Solution processes are thermodynamically equilibrium processes, and thus the precise control of growth process, impurity, doping and product uniformity are the major problems. In addition, chemical waste treatment also needs to be addressed to deal with the environment issues in the future for commercialization. However, from cost efficiency point of view, a low-cost chemical synthesis with high yield undoubtedly is suitable for commercialization of nanostructure materials. Several solutions based chemical synthesis methods are introduced below.

2.2.1.5 Chemical Bath Deposition (CBD)

The term of CBD is referred to the techniques that produce a solid structure in a single immersion through a control of the formation kinetics of the solid, normally without changing the metals’ oxidation states [131]. ZnO nanorods can be produce by CBD at a temperature as low as 60°C.

Vayssieres et al. used this method to grow ZnO nanorods in 2001 [132]. ZnO seeds are required to initialize the oriented nanowires growth. The solution containing ZnO(NO₃)₂ and hexamethyldetramine (HMT) is used, the PH value can vary from 5 to 12. The main reactions involved in this process are:

\[
\begin{align*}
\text{(CH}_2\text{)}_6\text{N}_4 + 6\text{H}_2\text{O} & \leftrightarrow 6\text{HCHO} + 4\text{NH}_3 \quad 2-2 \\
\text{NH}_3 + \text{H}_2\text{O} & \leftrightarrow \text{NH}_4^+\text{OH}^- \quad 2-3 \\
2\text{OH}^- + \text{Zn}^{2+} & \rightarrow \text{ZnO(s)} + \text{H}_2\text{O} \quad 2-4
\end{align*}
\]

The deposition rate is mainly dominated by HMT decomposition rate (reaction 1), which is strongly temperature dependent. Therefore, by adjusting reaction temperature, ZnO nanostructures with different feature can be obtained. The normal reaction temperature range is ranging from 60°C to 200°C [133]. ZnO nanostructures
such as nanorods [134, 135], nanowires [133], nanoplate [136, 137], and nanospheres [138] can be produced by varying the reaction temperature, solution pH value, Zn salt type, basic reagents, and additives. However, the ZnO nanostructures produced by this method normally do not have good adhesion to the substrate.

2.2.3.2 Electrochemical Deposition (ECD)

ZnO can be deposited cathodically from an aqueous solution of Zn salt in the presence of dissolved oxygen. Nano-rods, nano-tubes [139] and nano-porous film [140] have been successfully synthesized by ECD. The porous ZnO film is studied intensively for the DSSC applications. To produce porous ZnO films by ECD, shape-control reagents are commonly added to create desired porosity [141].

2.2.3.3 Sol-Gel Synthesis

ZnO thin films [142-147], nanocrystals [148], nanorods [149] with preferred crystallographic orientation have been synthesized using the sol-gel method. “Sol” is referred to a colloidal suspension. The formation of Sol will develop inorganic networks, and as the networks form in a continuous liquid phase, it becomes “gel”. The precursors for synthesizing these colloids consist of a metal/metalloid surrounded by various reactive ligands. Metal alkoxides are most popular because they react readily with water.

At the functional group level, three reactions are involved in the sol-gel process: hydrolysis, alcohol condensation, and water condensation. However, a number of factors such as PH, temperature and time of reaction, reagent concentrations, catalyst nature and concentration, aging temperature and time, and drying have impacts on the characteristics and properties of a particular sol-gel inorganic network by affecting the rate of hydrolysis and condensation reactions.
2.2.4 Limitations of Current Techniques

<table>
<thead>
<tr>
<th>Category</th>
<th>Techniques</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
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<td>High temperature</td>
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<td></td>
<td>Nanostructures variety;</td>
<td>Vacuum</td>
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<tr>
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<td></td>
<td>No chemical waste</td>
<td>Small scale</td>
</tr>
<tr>
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<td>Sputtering</td>
<td>Doping</td>
<td>High adhesion to substrate</td>
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<tr>
<td></td>
<td></td>
<td>Good adhesion to substrate</td>
<td>Low temperature capability</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Low temperature capability</td>
<td>Nanostructures difficulty</td>
</tr>
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<td>PVD</td>
<td>PLD</td>
<td>High quality</td>
<td>High vacuum</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Variety of products</td>
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<td>Precise control of composition</td>
<td>Expensive equipment</td>
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<td></td>
<td>PECVD</td>
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<td>Dimension and doping</td>
<td>Facility requirement</td>
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<td>CBD</td>
<td>Low temperature</td>
<td>Product quality, Uniformity</td>
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<td>Easy operation</td>
<td>Precise control</td>
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<td></td>
<td>Large variety of nanostructures</td>
<td>Environment issues</td>
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<td></td>
<td></td>
<td>High yield, Low cost</td>
<td>Doping problem</td>
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<td></td>
<td></td>
<td>Scale up capable</td>
<td>Bad adhesion to substrate</td>
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<td></td>
<td>ECD</td>
<td>Low temperature</td>
<td>Product quality, Uniformity</td>
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<td></td>
<td>Traditional method</td>
<td>Precise control</td>
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<td>SBC</td>
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<td>Easy operation</td>
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<td>Large variety of nanostructures,</td>
<td>Environment issues</td>
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<td>Low cost</td>
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<tr>
<td></td>
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<td>Scale up capable</td>
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</table>

Many methods have been used for deposition and growth of ZnO based thin films and low-dimensional nanostructures. Each of these techniques has its own
advantages and limitations. Table 2-4 summaries their pros and cons with respect to
the product quality, nanostructure synthesis ability, doping ability, experimental
facility requirement, operation complexity, scale-up potential, and issues related to
environment.

Generally, the gas phase approaches can produce a variety of high quality, single
crystal ZnO nanostructures, and doping is relatively easy to be achieved and
controlled. They however have high requirement on the vacuum level and most of
them operate at elevated temperatures. Therefore, the required instrument is
expensive, and it is hard to achieve the mass production. In some gas phase methods
such as MOCVD, toxic chemicals are used and will result in some environmental
problems. They are more suitable for scientific research in the laboratory scale. The
commercial products derived from these techniques will usually be expensive.

In contrast, the solution based methods are simple in operation, have minimum
requirement for facilities. Those methods are operated at a temperature much lower
than that of the gas phase methods, and thus are cost efficient and energy-wise. It is
also easy to scale up the production, and thus more ready for commercialization.
However, ZnO nanostructures produce by these methods generally have lower
quality than those from the gas-phase approaches. Defects and impurities are almost
incontrollable in this case. The same fact is also held for doping. Various chemicals
are needed to aid the nanostructures growth, which will be a major problem in the
future when the process is scaled up. Furthermore, the nanostructures grown from
the solutions normally do not have very good adhesion to the supporting substrates.
This is also a problem when these nanostructures are used for applications requiring
long life cycle and good networks between nanostructures and their substrates.

From the above discussion, it can be seen that despite the existing broad
techniques for ZnO nanostructure production, there are still some gaps left by the
current techniques to be filled, so that applications of ZnO nanostructures can be better realized. This is one of the main motivations for the work being described in this thesis research.

2.2.5 Wet Oxidation

Wet oxidation is not a new topic to material researchers. The metal oxidation in the presence of water vapour has long been studied in the area of high temperature corrosion and protection of metals and alloy [150, 151]. In semiconductor industry, wet oxidation is also an important processing technique, especially for the growth of SiO$_2$, an insulating layer for Si wafers. Introduction of a small about of water vapour into the oxidising atmosphere could significantly affect the oxidation and scaling behaviours of metals [152]. The growth of metal oxide in whisker type structure has also been observed back to 1980s [150-152]. It is also widely reported that the addition of water vapour could increase the plasticity of the formed oxide significantly. Therefore, this technique should be able to apply for ZnO nanostructures growth, and some work did earlier in our group have shown ZnO nanowires can be obtained by wet oxidation [153].

The ZnO films produced by thermal oxidation of Zn films, usually deposited by magnetron sputtering, have been studied by some groups, and it has been demonstrated that the ZnO films formed by oxidation have exhibit excellent PL properties [154-156]. It is also reported that $p$-type ZnO film can be produced by oxidizing Zn$_3$N$_2$ [87, 157-159]. Thermal oxidation can also be used to synthesize ZnO nanostructures [160-166]. However, most of these studies still need conduct the experiments at reduced pressure and high temperature conditions. Oxidation at 500°C to 600°C has been regarded as low temperature. In addition, Zn powder were commonly used in nanostructure related studies, and thus the products would have
the same weakness as those produced from other vapour approaches, e.g. free standing, poor adhesion with the supporting substrates. However, studies on the effects of introducing water vapour to the oxidation atmosphere to form ZnO nanostructure and producing ZnO nanostructures from oxidation of Zn films have been rarely reported.

The introducing water vapour to the oxidizing environment is known can greatly accelerate the oxidation reaction and therefore reduce the oxidation temperature. This is because the breakup of H$_2$O molecules is faster than that of oxygen molecules at elevated temperature. In the case of Zn oxidation, the Zn vapour transport distance is shorter than that of thermal CVD processes, and thus wet oxidation can be carried out at much lower temperature than most of the vapour based methods. Moreover, unlike the other vapour techniques which have to be conducted in vacuum chamber, wet oxidation can be done at ambient atmosphere, which significantly reduces the instrument requirement and cost. In addition, no toxic chemical is needed, and it is an environmental friendly method.

The ZnO nanowires grown from wet oxidation have comparatively good quality with those obtained from gas phase methods, and as the nanowires are grown out from the Zn precursor films, they should have good adhesion to the substrate. Therefore, wet oxidation is an economical method compared to the other expensive gas approach, and would be capable of producing ZnO nanostructures of better quality than the solution methods at the same time.

Nevertheless, the mechanism behind the formation of ZnO nanostructures in wet oxidation needs to be thoroughly studied before the growth of nanostructure can be precisely controlled. Doping methods are also needed to be developed for wet oxidation, so that the properties of ZnO nanostructures can be tuned to meet specific...
requirements. The works described in this thesis are an attempt to deal with these challenges.

2.3 Applications

ZnO offers a number of remarkable potential applications in chemical and physical areas. ZnO-based nanostructures hold a host of opportunities for flat screen displays, field emission sources, gas, chemical and biological sensors, and UV light emitters, detectors and switches. Here, a few examples will be demonstrated to show utilization of ZnO nano/micro-structures in the areas of photo-chemicals, photovoltaics and piezoelectric devices, which we believe are the most desirable applications for ZnO nanostructure grown from wet oxidation.

2.3.1 Light Emission

![Figure 2-9. SEM images of the single nanowire LED device, and light emission come from the device when a positive voltage (7 V) was applied [167].]

A primary motivation of the research on ZnO is developing ZnO based light emitting devices, and ZnO nanostructure based LEDs have been fabricated by different research groups using various techniques [167, 168]. Figure 2-9 shows the single nanowires LED device fabricated by Bao et al. and the light emission come
from the device. However, there are rarely reports demonstrating these devices can have good repeatability and long life time, mainly due to unstable $p$-type doped ZnO.

### 2.3.2 Solar Cell

The use of highly conductive transparent ZnO film as the transparent electrode of solar cell has been well established. The use of ZnO single-crystalline nanowire arrays as the photoanodes is a promising approach to improve the efficiency of the current DSSC. This is because, firstly the high aspect ratio nanostructures can provide a large surface area for the adsorption of the light-harvesting dye molecules; and secondly, the electron transport through these single crystal wires is expected to be several orders of magnitude faster than that by the random-walking mechanism associated with the nanoparticle film, which are currently used in the DSSC applications. The increase of the electron diffusion length may also allow for thicker cell with greater dye loading and the use of solid state electrolytes. In addition, if incorporating the ZnO nanowires with the ZnO transparent electrode, the good crystal lattice match between the photoanodes and the electrode should further improve the electron transport efficiency.

Yang’s group has firstly fabricated the DSSC based on the ZnO nanowire arrays grown from solution method [133]. Figure 2-10A shows their DSSC configuration, and Figure 2-10B is a plot of the current density versus voltage ($J-V$) for their two best devices. A full sun efficiency of 1.5% and external quantum efficiency (EQE) at ~40% were achieved by this setting. However, this result is obviously not good enough in comparison with best efficiency of more than 10% achieved by TiO$_2$ based DSSC [169]. The main limiting factor that prevents obtaining higher efficiency is that the ZnO nanowires have smaller roughness factor (~200) compared to the TiO$_2$ nanoparticles (~1000), therefore less dye molecules is absorbed to the
anode, and thus reduced the efficiency. Some researchers including those in our group are working on the ZnO/TiO$_2$ composite structures, and intending to solve this problem by combining the high electron transport of ZnO and good dye absorption ability of TiO$_2$.

Figure 2-10. A) Schematic diagram of the ZnO nanowire based dye-sensitized solar cell fabricated by Yang’s group. B) The current density versus voltage (J-V) plots for the device [133].
2.3.3 Nanogenerator

Figure 2-11. Design and electricity-generating mechanism of the fibre-based Nanogenerator driving by a low-frequency, external pulling force [170].
Wang’s group have intensively studied the piezoelectric properties of ZnO nanowires [10, 13, 18, 19], and have demonstrated the feasibility of collecting electrical power generated from ZnO nanowire by mechanical deformation. ZnO nanorods were also grown on Kevlar fibres, and electrical energy can be generated by relative motions between the fibres, a bright future was drawn where man’s clothes can generate electrical power from bio-motions [170].

Figure 2-11 shows the design and the electricity generating mechanisms of the fibre-based nanogenerator. While the actual realization of this idea may still have a long way to go, it does give an illustration about the potential of the applications utilizing the special properties of the ZnO nanostructures, which was beyond people’s imaginations in the past.

2.3.4 Environmental Applications

It has been reported that ZnO exhibited switchable wettability. An exposure to UV irradiation can turn the ZnO from hydrophobic (water contact angle > 90°) to hydrophilic (water contact angle < 90°), and storage in dark can convert ZnO back to hydrophobic. Research shows that nanostructures such as nanorods arrays can enhance this switchable wetting property, and exhibit the super-hydrophobic-hydrophilic behaviour (151° to 12°, before and after UV irradiation for ZnO nanorod array) [16]. This property is useful for environmental cleanup. Commercial products such as antifogging glass and self-cleaning construction materials (windows and walls) have already entered the market.

ZnO also have good photocatalytic properties. Its photocatalysis mechanism is similar to that of TiO₂. When exposed to UV light, electron-hole pairs are created by photons. The holes can react with H₂O and give hydroxide radical (OH•), and the electrons can react with absorbed O₂ to form oxygen radical (O₂•-), which can form
hydroperoxyl radical (HOO•) when react with hydrogen ion (H⁺) in water [171]. Both OH• and HOO• can oxidize and degrade the organic compounds due to their great oxidising power.

Compared to TiO₂, ZnO is easier to form a variety of nanostructures, which can provide larger surface area for absorption, and thus increasing the photocatalysis efficiency. Using ZnO nanostructures on supporting substrates can increase the re-usability of the catalysts. Problems such as the secondary contamination and recycling of catalyst materials related to nanopowders as catalyst can be significantly reduced.

2.4 Summary

ZnO has fascinating chemical, electric, optical, and physical properties. Various structures of ZnO, such as 1D nanowires, nanobelts, dense or porous films, and more complex 3D architectures, could be produced through chemical and/or physical routes. ZnO thus has great potential for the applications in electronics, photonics and catalysis. However, current ZnO synthesis techniques still have their limitations. Development of new or more reliable techniques is necessary to solve these problems, so that the superior properties of ZnO can be appropriately utilized in industrial applications.
CHAPTER 3. EXPERIMENTAL METHODS

In this chapter, the experimental works on synthesis of ZnO nanostructures by wet oxidation method are described, including equipment setup and nanostructure growth procedures. An introduction of characterization methods used in this thesis is given as well. Some special and detailed experimental conditions and processes will be introduced in the related chapters.

3.1 ZnO Nanostructures Growth

Two steps are used to produce ZnO nanostructures in the wet oxidation process. The first step is the preparation of metallic Zn precursor films, which is done by using magnetron sputtering in this thesis. The second step is wet oxidation process, to convert the metallic Zn precursor into ZnO nanostructures with different morphologies. Each of the steps is described below.

3.1.1 Magnetron Sputtering (MS)

The MS system used in our laboratory was a home-made instrument, which is initially designed for the study of hard, wear and corrosion resistant coating of metallic nature. Therefore, its configuration has some differences from the commercial available MS systems. However, it has the advantage of high deposition rate, and can be used to deposit both thin films and thick metal coatings. Figure 3-1 shows the picture of this MS equipment.

The target used in this system is ~15 cm (6 inches) diameter target, much larger than those used in commercial MS system, which allows large sized or more samples to be prepared in one batch. Two targets can be used for the sputtering at the same time. These two targets are placed parallel to each other, thus co-sputtering
experiment can be conducted, while for most of the work in this thesis, only one target is used.

*Figure 3-1. The unbalanced MS system used for Zn precursor films preparation.*

For the working gas supply system, high pure Ar gas is normally used as the working gas. In addition, another type of gas, such as N$_2$ and O$_2$ can be introduced into the chamber at the same time from a separate channel. The flow-rate of each gas and the total working pressure in the sputtering chamber can be adjusted simultaneously, so that doping or reactive sputtering can be performed on this homemade machine.

The substrates are loaded in the centre of the vacuum chamber, about 13cm away from the target. The substrate can be rotated in a controlled speed to ensure uniform deposition. A bias voltage can be applied to the substrate to assist the deposition and increase the adhesion of the film to its substrate. There is no heating
unit for the substrate in this system. Figure 3-2 is the schematic drawing illustrating the interior configuration of this MS setup.

![Figure 3-2. A schematic drawing of the configuration of inside the sputtering chamber.](image)

Both radio frequency (RF) and direct current (DC) power can be used in this system, so both conductive and insulating material can be used. RF power supply can be also connected to the substrate holder to perform plasma cleaning of the substrate prior to the deposition. A rotary pump and a diffusion pump are used to achieve the desired vacuum condition within the chamber. The background pressure
is normally $4 \sim 5 \times 10^{-6}$ Torr before the deposition starts. The chamber walls and the targets are cooled with flowing water to ensure safe operation, and there is an observation window for monitoring the sputtering process.

For the preparation of Zn precursor films, typically glass substrates with a size of $12 \text{ mm} \times 12 \text{ mm} \times 1 \text{ mm}$ cut from microscope glass slides were used. The substrates were ultrasonically cleaned in ethanol, acetone, and ethanol in sequence, and dried by hot air before loaded into the sputtering chamber.

After the chamber was pumped down to under $5 \times 10^{-6}$ Torr, high-purity Ar gas (99.999%) was introduced into the chamber, and the total pressure in the chamber was regulated at 20 mTorr. The substrate in the chamber could be further cleaned with high power plasma treatment by connecting to the RF power with frequency of 13.56 MHz to initiate a plasma plume around the substrate. The forward power of 500 W and reflected power of 40 W are normally used. After 1 hr plasma cleaning, the working gas pressure was changed to 10 mTorr for Zn precursor deposition. DC power was used as the Zn target (99.99%) is conductive. The current value can be increased from 0.1 A up to 0.75 A for Zn target. The Zn deposition rate is quite fast under the DC mode. Zn precursor films with the thickness of up to several microns can be deposited within 10 min. After the deposition, the DC power was switched off and the working gas system was close at the same time. Then the chamber was vented 30 min after the deposition, to allow the system being cooled down.

### 3.1.2 Wet Oxidation

Figure 3-3 shows the tube furnace used for the wet oxidation and the schematic drawing of the wet oxidation system. The oxidation of precursor film is performed in the quartz tube heated by an electrical resistor furnace. The end of the tube was sealed during the oxidation to maintain the oxidation atmosphere within the tube.
Chapter 3. Experimental Methods

The design of the tube allows the oxygen to flow directly to the high temperature zone where the reaction takes place, and flow out at the low temperature end with a water seal. A flowmeter was installed at the inlet stream to control the O₂ flow-rate. The wet oxidation is conducted at the ambient pressure, so no vacuum or pumping is needed.

![image](a)

Figure 3-3. a) A photo showing of the tube furnace used for wet oxidation process, and b) the schematic drawing showing the whole wet oxidation system.
Chapter 3. Experimental Methods

The to-be-oxidized specimen was connected to one end of a steel rod, and a magnet was tied to the other end. By using another magnet outside the tube, the specimen could be moved along the tube without opening sealing.

In a typical wet oxidation process, the dry O₂ was firstly bubbled through a water flask containing deionised (DI) water, so that the O₂ could carry water vapour into the tube for conducting wet-oxidation. The pipe connecting the water flask and the tube was wrapped by heating ribbon to prevent water vapour condensation. A thermal couple was used to monitor the temperature on the pipe surface. The water flask was kept in a water bath of constant temperature. The amount of water vapour carried into the tube was controlled by the water bath temperature. For example, at 45⁰C the vapour pressure of water is 9595 Pa [172], and the mole fraction of water is air is 9.47% according to Equation 1:

\[
y = \frac{p_v}{P}
\]

Where \( y \) is the mole fraction of water (mol•mol⁻¹):

\( p_v \) is the vapour pressure and

\( P \) is the total pressure of the gas phase. [172]

Before oxidation started, the specimen was placed at the cold region of the tube, and O₂ was introduced at a flow-rate of 0.6 L/min for 40 min to flush out the air in the tube and maintain a highly oxidizing atmosphere in the tube. Meanwhile, the furnace and the water bath were heated to the desired temperature. The O₂ flow-rate was then turned down to lower value, and the specimen was moved inside the furnace to the high temperature zone to initialise the wet oxidation process. The oxidation temperature was around the melting temperature of Zn (420 °C), and the oxidation time was varied from 1 hr to 16 hr for different samples. After oxidation,
the supply of oxygen was stopped, and the specimen was removed after cooling down.

### 3.2 Characterization Methods

Microstructure characterizations of Zn precursor films and thermal grown ZnO nanostructures were carried out using a variety of modern facilities. High resolution field emission gun scanning electron microscopy (FEG-SEM, Philips XL-30S at 5 kV) and energy-dispersive X-ray spectroscopy (EDX at 15 kV) were used to investigate the surface and cross section morphologies as well as the micro-compositions of samples. High resolution transmission electron microscopy (HRTEM, JEOL JEM-3010 operating at 300 kV) was used to investigate the crystal lattice in more details and powder X-ray diffractometer (XRD, Bruker D8) with Cu-Kα radiation were used to characterize the crystal structures.

The chemical states of doping elements in the ZnO nanostructures were investigated by photoelectron spectroscopy (PES) experiments based on synchrotron radiation at the Australian Synchrotron Centre (soft X-ray beamline with photon energy of 90-2500 keV). The X-ray photoelectron spectroscopy (XPS) spectra obtained with synchrotron radiation are much clearer and the element concentration limit to be detected is also much lower than those obtained with laboratory based XPS, due to not only the high photon flux, but also the selectable excitation energy, which can be adjust to maximize the excitation cross section [87].

Photoluminescence (PL) measurement with the He-Cd laser source of 325 nm is a suitable and commonly used tool to investigate the optoelectronic property of ZnO material. Much useful information such as the crystal quality, band gap structure and the presence of impurities and doping elements in ZnO materials can be directly displayed from the PL testing results [8, 47, 67, 173]. PL measurement results
indicated that single ZnO crystal film or nanostructures could produce very strong UV light emission [174] and demonstrate great potentials for electronic and photonic applications, which has probably been one of the primary reasons that ZnO could attract such intensive research attention worldwide these days. For the current thesis research, low temperature and room temperature PL testing have been carried out on the nanostructures produced by wet oxidation for specific purpose. The intensity dependence and temperature dependence PL measurements have also been studied in details.

Optical properties of ZnO nanostructures were also studied by means of micro-cathodoluminescence, UV-vis absorption and reflection measurements. The cathodoluminescence (CL) characterization was performed using in-situ Gatan Mono CL2 system in a FEI Quanda 2000 environmental scanning electron microscope (ESEM). The CL signals were collected using a Czerny-Turner monochromator with a Peltier-cooled Hamamatsu R943-02 photomultiplier UV-vis detector. CL tests can collect the spectra from the selected locations [175-177]. UV-vis absorption measurement was conducted with a UV-vis spectrophotometer (Agilent 8453), and the reflection measurement was conducted by a Shimadzu 2100 UV/vis instrument.
CHAPTER 4. FABRICATION OF ZINC OXIDE
NANOSTRUCTURES BY WET OXIDATION

4.1 Introduction

This chapter focuses on the ZnO formation process of ZnO in the wet oxidation and the related growth behaviour. The experiments indicated that during the formation of ZnO nanostructures, lots of parameters or factors, such as the initial zinc (Zn) precursor structures, oxidation time, temperature, water vapour concentration, and O₂ flow-rate, have important effects on the final ZnO products. Thus for the current study, the microstructure, phase structure and optical properties of as-grown ZnO nanostructures have been systematically investigated, which provided a better understanding of the ZnO nanostructure growth mechanisms during the wet oxidation, and showed the way to achieve controllable ZnO nanostructures growth with high efficiency.

4.2 ZnO Nanostructure Growth Mechanisms

4.2.1 Zn Precursor Film Deposition

Previous study showed that the specific structure of Zn precursors was critical for nanowire formation in the later stage. The special Zn features obtained from magnetron sputtering (MS) could be directly converted to ZnO at the beginning of oxidation, and then served as nucleation sites for the growth of ZnO nanostructures by preferentially capturing Zn vapour species [178]. The influences of sputtering parameters especially the deposition time on the Zn precursor structures were studied in this session.
4.2.1.1 Experimental Procedures

The Zn precursor films were prepared by direct current (DC) MS as described in Chapter 3.1.1. Deposition time was varied from 1 to 10 min when the deposition current was fixed at 0.5 A in order to evaluate the influence of deposition time on the Zn precursor structure. The deposition current of 0.25, 0.6 and 0.75 A was also used for the deposition after the optimum deposition time was found. During the deposition the substrates were rotated at a speed of 3 rpm with an applied bias voltage of -50 V.

The surface and cross-section fracture morphologies of the as-deposited Zn precursor films were characterized with scanning electron microscopy (SEM) operating at 5 kV, while their crystal structure was analyzed with X-ray diffractometer (XRD), as described in Chapter 3.

4.2.1.2 Results

The microstructures of Zn precursor films with different deposition time were investigated by SEM, and the typical surface morphologies of the Zn films with the deposition time increasing from 1 to 10 min were shown in Figure 4-1. Particles with various grain sizes were observed. The minimum, average and maximum grain size values were statistically analyzed by using SEM graphical analysis software (Scandium) and the related results were plotted in Figure 4-2. It can be observed that the plot shows two obvious jumps in grain size values for the Zn precursor films with the deposition time of at 4th-5th min and 8th-9th min, implying that the Zn precursor growth can be divided into three stages.
Figure 4-1. SEM images of Zn precursor with deposition time of a) 1 min, b) 3 min, c) 5 min, d) 8 min, e) 9 min, and f) 10 min.

Three distinct layers can also be observed from the cross section of the sample grew for 9 min (Figure 4-3b). The thickness of the first layer on the 9-min sample is similar to the total thickness of the sample after 3 min deposition (Figure 4-3a). The first layer of Zn grains, therefore, playing the role of the contact layer between the glass substrate and Zn, can be called the buffer layer for the growth of metallic Zn.
Figure 4-2. The plot of minimum, average and maximum Zn precursor grain size, measured from SEM image of samples with deposition time from 1 min to 10 min.

Figure 4-3. SEM image of the cross-section of Zn precursor films with deposition time: a) 3 min, and b) 9 min.

The first layer shows a large peak shift in XRD patterns in Figure 4-4: the (002)\textsubscript{Zn} peak shifted ~0.18° towards the high angle side from the standard value (36.30°). The large peak shift could be the result of many factors such as frozen in defects, or thermal expansion difference with the glass substrate. The second Zn layer was grown on top of the first Zn layer, and therefore the stress between the two layers was much smaller. It can be seen that the Zn grains grew larger with improved crystallinity. The third layer grew up from the second layer, forming even
larger Zn crystals. The peak shift from the standard value (36.30°) generally decreased with increasing deposition time, indicating the decreased interfacial stress as well as improved crystal structures. The small increases of peak shifting at 5 and 9 min positions probably indicate the formation of the new grain layer (Figure 4-5).

**Figure 4-4.** XRD patterns of Zn precursor films with deposition time of 1 min, 3 min, 5 min, 8 min, and 9 min.

**Figure 4-5.** Zn (002) peak shifting related to the standard position.
4.2.1.3 Discussion of the Zn Precursor Growth with Deposition Time

From the results described above, it can be seen that the Zn precursor growth can be divided into three stages within the 10 min deposition time, which have been labelled in Figure 4-2. The first four min was Stage-1, where the Zn started nucleation on the substrate and formed irregular shape grains with an average size of 50 nm (ranging from 20-100 nm) in the 1st min (Figure 4-1a). The nucleation continued to 3rd min, where the grain size was doubled (Figure 4-1b). Hexagonal-like particles can be occasionally observed on the 3-min sample, which suggests that the second layer of Zn has started to grow.

When the deposition time increased to 5 min, hexagonal-shaped grains almost covered the surface, which was the start of the second stage. A micrograph of a Zn particle was taken at a higher magnification, and is shown on the up-right corner of Figure 4-1c. it can be seen that the particle surface is very rough with many small tips on it, and these small tips were described as the initial ZnO nucleation site [178], and thus are supposed to be important for ZnO nanowires growth. During Stage-2 (5 to 8 min), the Zn particle size gradually increased while maintaining its hexagonal shape (Figures 4-1c and 1d).

It can be seen from Figure 4-2 that the maximum grain sizes of 8-min and 9-min deposited samples are similar, but the average grain sizes are quite different. The fact that some exceptionally large grains appeared on the 8-min samples indicates that the Stage-3 growth initiated at the 8th min. For the film after 9 min deposition, most of its surface has been occupied by large grains with the diameters of ~500 nm (Figure 4-1e). After 10 min deposition, the 3rd layer of Zn formed with closely packed grains (Figure 4-1f).
4.2.1.4 Conclusion

Zn precursor growth consists of three stages. From the second stage, hexahedral shape Zn particles appear with small tips feature on the particle surface. According to the previous study, Zn precursors with deposition time longer than 5 min should favour the ZnO nanowires growth, which is going to be discussed in Section 4.2.2.

4.2.1.5 Deposition Current Influence

In the above study about the influence of deposition time, only 0.5 A was used for the DC sputtering. The deposition current has major influence on the surface morphology, as the higher the current is, the higher energy the incident depositing atoms have, and the higher deposition rate. So deposition Zn with different current value was carried out. The deposition time was 5 min, and other conditions were the same as the previous section. The deposition currents used are 0.25 A, 0.6 A, and 0.75 A, apart from 0.5 A.

4.2.1.6 Results and Discussions

Figure 4-6 shows the surface morphologies of the Zn film obtain at 0.25 A, 0.6 A and 0.75 A, with the same deposition time of 5 min. At 0.25 A, Zn did not form hexahedral shape Zn particles as those formed at 0.5 A with the same deposition time. Instead, irregular shape grains connected by wire-shape crystals formed a porous network. This type morphology is typical for partial oxidized Zn film which will be discussed in Chapter 7. This indicates that at lower deposition current, 0.25 A, some Zn could be oxidized during the deposition, even though no oxygen was intentionally introduced into the chamber. The oxidation source could be the absorbed O$_2$ on the inner surface of the chamber or O$_2$ in the residual gas molecules.
Figure 4-6. SEM images of Zn precursor with 5 min deposition time at a) 0.25 A, b) 0.6 A, and 0.75 A.
The reason of the oxidation is not clear, but it could be due to that at low current, the Zn atoms came out from the target with lower kinetic energy, and would take more time to reach the substrate, and thus have higher possibility to react with the residual O₂. Moreover, the oxidation may also happen for a higher current, but at a high current the deposition rate is much higher. Therefore, the residual O₂ may be consumed in a short time, and the total percentage taken by the oxide is too low to affect the structures.

The film obtained at 0.6 A current (Figure 4-6b) has the similar morphology with that from 0.5 A (Figure 4-1c), only that the particle size seems larger, but the increase is not significant. Deposition at 0.75 A gave similar particle size, but more small tips can be observed on the particle surface. These tips should favourable for ZnO nanowires growth.

This study of the current effects on the Zn morphologies demonstrated that Zn particles with desired features could not form at low current. Increasing current above 0.5 A could slightly increase the particle size and form small tips on the particle surface, which would benefit the ZnO nanostructure growth in the wet oxidation process, as the similar effect as increasing deposition time. However, with high current, the deposition voltage would increase dramatically. Sparks could be observed on the target surface sometimes, and the heat generated at the target and magnet was high, which may damage the MS system. Therefore, 0.5 A was still chosen for the rest experiments.
4.2.2 Influence of Zn Precursor Structure on ZnO Nanowires Growth

Zinc precursor films deposited by DC-MS with deposition time of 1 to 10 min were wet-oxidized with the same condition to found the optimum Zn precursor structures for ZnO nanowires growth.

4.2.2.1 Experimental Procedures

Wet oxidation process followed the same treatment routine as described in Chapter 3.1.2. The Zn precursors studied in the previous section were oxidized at 420°C with oxidation time of 4 hr. The oxygen flow-rate was 0.3 LPM, and water bath temperature was kept at 45°C.

4.2.2.2 Results and Discussions

Figure 4-7a shows the morphology of ZnO formed from the 1-min deposited Zn film after wet oxidation. The inserted image is the corresponding Zn precursor before oxidation. Other photos in Figure 4-7 are arranged in the same way. The Zn film was oxidized to form a dense ZnO film. Some tiny ZnO nanorods can be occasionally observed on the surface, with lengths of less than 300 nm. More nanowires with greater length can be seen on the 3-min Zn film after wet-oxidation, many of which have a length exceeded 5 μm (Figure 4-7b). Most of the nanowires initiated their growth from the protruding parts of the Zn grains, which correspond to the occasionally spotted hexahedron-shaped grains in Figure 4-1b.

The morphologies of ZnO that formed on Stage-2 Zn films (5 to 8-min deposition) does not vary much across the time period, but the nanowires have a much higher population and are longer than those from the Stage-1 samples (Figure 4-7c& 7d). Figure 4-8a shows the cross section view of 8-min Zn after oxidation, exhibiting the porous structure of the film. The pores in the middle of the film are
evidences of the evaporation mechanism, which will be discussed later in Section 4.2.5.2.

Figure 4-7 SEM images of ZnO nanostructures formed after 4 hr wet oxidation at 420°C using the Zn precursors with different deposition time: a) 1 min, b) 3 min, c) 5 min, d) 8 min, e) 9 min, and f) 10 min. The O₂ flow-rate for the wet oxidation process was kept at 0.3 LPM. The insert small photo on each one shows the morphologies of the precursors before oxidation.

At the Stage-3 Zn films showed a different ZnO structure. The morphology of the ZnO formed from the 9-min Zn film is similar to that of the 8-min sample (Figure 4-7e), as the gaps between Zn grains are still large for 9-min Zn film.
Figure 4-8. SEM cross-section images: a) 8 min Zn and b) 10 min Zn, after 4 hr wet oxidation at 420°C with O₂ flow-rate of 0.3 LPM.

However, the number and length of ZnO nanowires grown out from the 10-min Zn films decreased dramatically (Figure 4-7f). This may be due to the decrease of porosity, which means that the oxides formed on the surface would block the spaces
between grains soon after oxidation started, and then slowed down the diffusion of oxygen to the inner layer of Zn and Zn vapour rising out of the film, resulting in slow and incomplete oxidation. Figure 4-8b is the cross section view of the 10-min Zn sample after oxidation. Oxide scale formed on the top of this film can be observed.

4.2.2.3 Conclusion

The result from the previous section shows that with the same oxidation conditions, Zn precursor films with deposition time of 5 to 9 min yielded most abundant ZnO nanowires. From the study of Zn precursor film in Section 4.2.1, it can be seen that 5 to 9 min deposition time just lies in the second stage of the Zn precursor growth, where hexagonal shape Zn particles appears with small tips on the particle surface. This also agrees with the previous results. Therefore, it can be concluded that in order to produce high abundant ZnO nanowires by wet oxidation, Zn precursor films need to have specific structure, which can be achieved by controlling the sputtering deposition time. As applied to our system, deposition time between 5 to 9 min are appropriate for the initial Zn precursor deposition by DC sputtering with the current of 0.5 A.

4.2.3 Influence of Oxidation Time

Wet-oxidation time is another important factor that affects the final ZnO nanostructures. The Zn precursor film with the deposition time of 8 min was used for testing how ZnO nanowires growth develops with increasing oxidation time. The wet oxidation conditions were the same as the previous section except for the oxidation time, which was varied from 1 hr to 16 hr.

4.2.3.1 Results and Discussions
Figure 4-9a shows the surface morphology of the 8-min Zn precursors after 1 hr oxidation. At this stage, ZnO nanowire growth had just started, the diameter and length of the nanowire were still small, and the distribution density was low. When the oxidation time increased to 3 hr, the average lengths of the nanowires are much increased, with most being over 10 μm. It appears that the majority of the nanowires grew in the same direction (Figure 4-9b). The similarity of growth orientation may be caused by the O₂ flow direction. This growth trend continued at the 5th hr since the sample surface had been fully covered by nanowires of great length and with high density (Figure 4-9c). However, at this point, nanowires did not grow in any preferential directions. Instead, most of the nanowires on top of the surface were curled and entangled with each other. This phenomenon is probably attributed to the interaction between the long nanowires and the gas flux. When the length and density of the nanowires increased, they started to interact with the gas flow which
may form local turbulence around the nanowires. Therefore, Zn vapour did not go straight along the direction of the main gas flow.

The growth rate slowed down after the 5th hr. The length and population of the nanowires on samples after 6 hr deposition showed little difference to the previous one. Further extension of oxidation did not favour the nanostructure growth, because the top of the film had been fully covered by oxide, and further growth of ZnO is difficult. However for Zn precursor with shorter deposition time such as 7 min, all Zn metal would have been fully oxidized into ZnO before the ZnO scale on the top of film start to inhibit the nanowire growth. It was also observed that if the sample was exposed in the same condition with a longer time, such as 16 hr, the nanostructure would be damaged (Figure 4-9d).

4.2.3.2 Conclusion

The oxidation time dependent study demonstrated that there was an optimum time in wet oxidation for the maximum growth ZnO nanowires. With shorter oxidation time, ZnO nanowire would keep growing, as there was enough Zn species to consume, and the oxide scale on the surface has not started to inhibit the ZnO formation process. For time longer than the optimum point, ZnO nanowire growth was not favourable. If exposed at a high temperature for a too long time, the nanostructure could be degraded.

4.2.4 Influence of Oxidation Temperature

The wet oxidation temperature is also a sensitive parameter for final ZnO nanostructures. Zn vapour pressure varies a lot at the temperature range around its vapour point, and it was suggested that ZnO nanostructure growth by wet oxidation follows the vapour–solid (V-S) mechanisms as described in Section 2.2.1.1. Therefore, the temperature dependence study should give important information.
about the ZnO nanowire growth mechanism in wet oxidation. Zn precursor films with 8 min deposition time were used in this section, and the samples were wet oxidized at 380°C, 420°C and 450°C. The other experimental conditions were the same as in Section 4.2.2.

4.2.4.1 Results and Discussions

The wet oxidation temperature is also a sensitive parameter for final ZnO nanostructure. Experimental results showed that dense and long ZnO nanowires or nanobelts could only be obtained within a temperature range from 380 to 450°C. If the oxidation temperature was lower than 380°C, no nanowires could form, although some thick ZnO blades might exist at 380°C (Figure 4-10a). At this relatively low temperature, most Zn would not be vaporized. They could only be oxidized to ZnO clusters in solid state.

The change in morphology can be explained from different aspects. Firstly, the Zn equilibrium partial pressure is 5.39 Pa at 380°C [2], much lower than that at 420°C (21.39 Pa). Therefore, if the V-S mechanism played an important role in the ZnO nanowire formation during the wet oxidation process, there were not enough reactants to keep the nanowire growth. Thus at this temperature, Zn diffusion should be the dominant mechanism for the thick Zn blade oxidation, rather than the V-S process. Secondly, the nanostructure growth was also enhanced by water vapour, because with dry oxygen, only flat oxide film can form during Zn oxidation [178]. It is reported that the Zn hydrolysis rate is relatively low below 400°C [179]. Therefore, at 380°C, the Zn-H₂O interaction was so weak that it could not assist the nanowire growth, which could be another factor resulting in the difficulty of getting large amount of ZnO nanowires at this temperature.
Figure 4-10. SEM micrographs of ZnO formed by oxidation of Zn under: a) 380 °C, and b) 450 °C.

When the oxidation temperature increased to 450°C, many long nanobelts formed during oxidation. However, the total population of the ZnO nanostructures was not as high as those from 420°C, as shown in Figure 4-10b. It is interesting to
note that some nanobelts were formed by two nanowires joining together and later separated again (Figure 4-11). At 450°C, the vapour pressure of Zn reached 48.9 Pa [2]. The high vapour supersaturation caused the morphological instability, and thus promoted the V-S process. In this case, ZnO would not only condense on the existing nucleation site such as nanowire tips, but also other random sites even the energy required for formation was higher.

Figure 4-11. Two narrow wires jointed together to form a belt and later separated again.
Among these sites, the positions between two adjacent nanowires should be preferred, as condensing ZnO and filling the gaps between two nanowires has less surface energy change than growing a new structure. Thus, the nucleation and growth of ZnO started between the closely located nanowires to form nanobelts.

As the oxidation process coming to the end, most of Zn metal in precursor film would be consumed by either oxidation or evaporation. Therefore, the supply of Zn vapour was reduced, thus the supersaturation level dropped, which stopped the growth of ZnO between nanowires. Hence, parallel branches can also be seen on the end of nanobelts.

Not all nanobelts were formed by joining nanowires in the middle of the process. Many of the nanobelts seem to have started growth at the beginning, but the observation of nanowires joined to form nanobelts can give some clues of the nanobelt formation mechanism, which will be discussed in Section 4.2.5.1

It has been noted that 450ºC is above the melting temperature of Zn (419.58ºC) [2]. Although the surface of many Zn grains would be oxidized before melting, allowing the small platelet structure to act as nucleation sites, some others would melt before being oxidized. Therefore, oxidation at a temperature above 450ºC would reduce the density of nucleation sites and change the oxide structure feature, resulting in the formation of ZnO nanostructures being less favoured.

### 4.2.4.2 Conclusion

The temperature dependence study indicated that the temperature was the major influential factor for altering the ZnO nanostructures. At a lower temperature, 380ºC, a few short and thick ZnO blades were formed with majority of the Zn turned to ZnO in bulk form. At the Zn melting point, 420ºC, ZnO nanowires with large populations could be obtained, and at a higher temperature, 450ºC, many ZnO
nanobelts could be seen from surface of samples. This study also offered some hints for understanding of the ZnO nanowire growth mechanisms in wet oxidation.

4.2.5 Discussions on the ZnO Nanostructure Formation Mechanisms

4.2.5.1 Role of Water Vapour

The previous work showed that oxidation of Zn films in dry oxygen only produced films with densely packed ZnO grains [180], and the involvement of water vapour for non-planar growth of oxide in metal oxidation has been reported for a number of metals [150]. It is suggested that the non-planar growth along the axis promoted by water vapour is a surface diffusion dominant process [150], the formation of multiform ZnO nanostructures in wet oxidation process is therefore not a simple V-S process. The growth of ZnO nanowires along a preferential direction needs nucleation sites to start. For the wet oxidation process, these nucleation sites were likely to be shaped from the small platelet structure on the surface of Zn grains, but the main reaction probably occurs between Zn and absorbed water vapour rather than O₂, according to the reaction below:

\[
\text{Zn} + \text{H}_2\text{O} = \text{ZnO} + \text{H}_2
\]

This is because, firstly, the water molecule has polarity. Its negative dipole (O side) is likely to be attracted by the Zn atoms on the surface and thus react with them to form ZnO. Secondly, it is believed that the breakup of H₂O molecules is faster than that of oxygen molecules at this temperature range [179]. As the surface diffusion is much faster than lattice diffusion, the breakup of oxidant gas molecules becomes the bottleneck at the initial nanowire growth stage, and the fact that the formation of ZnO nanowire is not favourable during the common dry oxidation of metallic Zn precursor proves that the breakup O₂ is slower than that of H₂O.
Figure 4-12. The schematic drawing illustrates the initial stage of wet oxidation on the Zn precursor particle surface: (1) the water molecule is attracted and absorbed to the Zn platelet structure, (2) water molecule breaks up to release hydrogen and oxidize the Zn, and (3) ZnO formed.
It is also reported that Zn hydrolysis rate is relatively low below 400°C [179], and our experiment results showed that below 400°C, such as at 380°C, nanowires did not grow well. At 420°C, wet-oxidation process reached the optimum condition. This suggests that the formation of ZnO nanowires is directly related to Zn-H₂O reaction rate.

In wet oxidation process, the fast absorption and easy breakup of water vapour can accelerate the kinetics of oxidation, which enables some of the Zn surface structures to transform to the nucleation sites for ZnO nanowires, as shown in Figure 4-12.

Figure 4-12. An illustration of the growth process of ZnO nanowires in wet oxidation process when the Zn surface diffusion is dominant the process: (1) Zn atoms diffuses to the growth front, and (2) fast reaction with water to form ZnO.

The Zn atoms surface diffusion and reaction with absorbed water vapour will continuously dominate the nanowire growth after the nucleation sites are formed as shown in Figure 4-13. This will only stop when the nanowires become too long for the Zn atoms to diffuse to the tips, or the diffusion tunnels become inactive. At this
stage, The V-S mechanism can take over to keep the nanowires to grow, as described by Figure 4-14.

Figure 4-14. An illustration of the growth process of ZnO nanowires in wet oxidation when the ZnO nanowire becomes too long for Zn diffusion, and V-S process becomes dominant: (1) Zn vapour from the Zn precursor film, (2) reacts with O₂ and form ZnO molecule, and (3) ZnO molecule condenses on the energy favoured site of existing ZnO nanowires.

The effect of wet-oxidation temperature on the oxidation behaviour supports the above mechanisms. On one hand, at temperatures below 400°C, the Zn-H₂O reaction rate is relatively slow. Therefore, at 380°C the Zn-H₂O reaction (Step 2 in Figure 4-
12) would not take place in time, thus the platelet structure on the Zn grains may be destroyed before being converted to the ZnO nucleation sites.

Figure 4-15. A schematic drawing for the formation of a nanobelt at high temperature.

On the other hand, At 450ºC, the Zn-H₂O reaction is enhanced compared to that at 420ºC. As a result, more platelet structures on Zn grains can be oxidized to form nucleation sites. As illustrated in Figure 4-15, the Zn platelet B may be also oxidized at the same time with Zn platelet A, which is less likely at 420ºC. When nanowires start to grow out from these two sites, the convex site between them will have low chemical potential for ZnO condensation [122]. ZnO will be more likely to condense
onto these sites and fill them. The two wires are then joined to form a belt, so that the nanobelts can start to grow from the root. This follows the same principle described in Section 4.2.4.1 about joining two nanowires to form nanobelts.

Another effect of water vapour is that water vapour may improve the plasticity of the oxide [152]. During SEM study, it was often observed that the ZnO nanowires or nanobelts could be deformed by electron beams to a high degree without being broken. However, as the nanowires were moving all the time during the bending deformation, a clear SEM image could not be taken to record this phenomenon.

4.2.5.2 Role of V-S Mechanism

The effects of Zn precursor structure on ZnO nanowire formation give an indication of how the V-S mechanism affects the nanowire growth. Figure 4-16 is a schematic illustrating the oxidation process of the Zn precursor film during each stage. Zn has a high vapour pressure of 21.4 Pa at the melting point of 420ºC. Therefore, a significant amount of Zn would be evaporated and then oxidized in the O₂ containing atmosphere to form ZnO in gas phase, which is then condensed to form ZnO nanostructures. However, Zn can also be oxidized or melted before evaporation. Three processes compete with each other, resulting in the different morphologies of ZnO formed at different stages.

At Stage-1 (1-4 min Zn deposition), the Zn precursor film is thin and the grain size is small, so the interface area to volume ratio is large, providing a large number of diffusion paths for O₂. Thus, when Stage-1 Zn precursors are exposed to the wet-oxidation environment, Zn can be easily oxidized before evaporation. Once the outer surface of the precursor is fully covered by ZnO, the contribution of Zn vapour to the growth of ZnO nanostructures becomes small (region A in Figure 4-16). Although Zn atoms can also diffuse out and then be oxidized, the diffusion rate is
slower than Zn evaporation. Therefore, the occasionally observed ZnO nanorods (Figure 4-7a) eventually formed are short. Due to the absence of platelet structure on the first layer of Zn gains, there are no significant nucleation sites for nanowire growth, which is the other reason that nanowires cannot grow from the first layer film.

Figure 4-16. A schematic showing the effects of Zn precursor structure on the V-S process.

1. First layer particle surface fully oxidized in a short time
2. Small tips being oxidized to become nucleation sites by water vapour;
3. Zn being vaporized;
4. Zn vapour meets oxygen;
5. Forming ZnO;
6. Condensation on ZnO nanowire tip, nanowire grow; and
7. Small gap is blocked by ZnO.

When the second layer Zn forms at Stage-2 (5-8 min deposition), the hexagonal-shaped grains on top of the film have thin platelet features on the surface. During the
wet oxidation, some of these tips are oxidized by water vapour to become nucleation sites for ZnO nanowires, and continue to grow to a distance by surface diffusion as discussed in Section 4.2.5.1. Following this, the V-S process becomes dominant. For the Zn precursor with a deposition time of more than 5 min, the film is thick enough that a significant portion of Zn can be evaporated before being oxidized, because the O$_2$ concentration at the base of the film is much lower than that at the film surface. As the second layer of Zn is loose, and pores exist between Zn grains, Zn vapour from inside of the film can come out through the gaps and pores to the surface where O$_2$ concentration is high. Zn can be then oxidized in the vapour state, which may be captured by the nucleation sites or the tip of existing nanowires, growing to long ZnO whiskers as illustrated in region B of Figure 4-16. The porous structure in the middle of the 8-min film (Figure 4-8a) is an evidence of the evaporation mechanism.

The Zn grains on the third layer (started to oxidize from the 8$^{th}$ min) are much larger than those on the first and second layers. When they become fully grown, for example the sample with 10 min deposition shown in Figure 4-1f, the Zn grains are closely packed, the gaps between them are smaller compared with the second layer, which will slow down Zn evaporation and thus the growth of nanowires (region C in Figure 4-16). This can be accounted for the phenomenon that 10-min Zn samples did not yield a high population of ZnO nanowires.

4.2.5.3 More Evidence for the Growth Mechanisms

Wet oxidation with lower flow-rate and higher vapour concentration was also carried out to check the feasibility of the proposed growth mechanisms. Figure 4-17a shows the morphology of ZnO formed by wet oxidation of Zn at 450°C with the flow-rate of 0.1 LPM, and other experimental parameters (e.g. oxidation time, water vapour % and precursor conditions) were the same as those used to produce the
sample shown in Figure 4-10b. Compared to Figure 4-10b, it is obvious that the population, length, width of the nanowires all decreased at flow-rate of 0.1 LPM. With a lower flow-rate, both the supply of the water vapour and O₂ were reduced. The reduction in nanowire population and number of nanobelt should be attributed to the short supply of water vapour, because water vapour has direct effects on the formation of the nucleation sites, as discussed in Section 4.2.5.1. The reduction of the nanowire length should be result from the short supply of O₂, because less O₂ means less ZnO species would be formed to continue the V-S process, which has the major impact on the later stage of the nanowires growth.

Figure 4-17. SEM micrographs of ZnO formed by oxidation of Zn at 450 °C with a flow-rate of 0.1 LPM.
Some secondary structure can be observed on the nanowires, especially on the tips. This should be also caused by the short supply of O$_2$. As mentioned in Section 4.2.4.1, Zn has a very high vapour pressure at 450°C, so the Zn supply should be adequate. But at 0.1 LPM O$_2$ flow-rate, some of the Zn vapour might not be oxidized in time, and re-condensed, some of which would captured by the nanowires. These Zn fell on the nanowires in metallic Zn form, so they would not have lattice match with the ZnO nanowire, therefore could not go to the energy preferential site of the existing ZnO crystals. Those secondary structures shown in Figure 4-17 b & c should be resulted from Zn, which re-condensed on the nanowires and then oxidized eventually in the oxygen rich environment.

With the temperature of water bath increased to 75°C, the water vapour pressure rose to 38.4 kPa [172]. According to Equation 3-1 presented in Section 3.1.2, the water vapour concentration in gas phase should be 37.95%, and the O$_2$% was then reduced to 62.05%. According to the discussions in Section 4.2.5.2, more water vapour should favour more nanowires nucleation sites, and less O$_2$ concentration should limit the V-S process and hence shorten the length of the nanowires. Figure 4-18a is the low magnification image of the morphology after wet oxidation with water bath temperature increased to 75°C. It appears that the nanowire population was significantly reduced. Whereas, viewing in higher magnification, there are many short rods grown out from a cluster. This observation agrees with the discussion above. The high concentration of water vapour promoted the nanowire formation, but the low concentration of O$_2$ prevented them from growing longer.
4.2.5.4 Conclusion

Based on the discussions above, a suggested growth mechanism of ZnO nanostructure can be drawn: The growth of ZnO nanowires by wet oxidation is a combined process of water vapour assisted surface diffusion of Zn atoms and V-S
process. The interaction of water vapour with Zn precursor has major influence on the density and feature of ZnO nanostructures. The duration of the V-S process has major effects on the final lengths of the nanowires and nanobelts, as well as their distribution density.

4.3 Characterizations

The crystal structures were closely studied by a high resolution transmission electron microscopy (HRTEM) for its lattice structure and growth orientation. Optical properties of the ZnO nanowires was characterized by cathodoluminescence (CL) and photoluminescence (PL) measurement to determine the crystal quality and band gap structures of the nanowires.

4.3.1 TEM Study

![Figure 4-19. TEM and Fast Fourier Transform (FFT) images of a nanobelt formed at 420°C for 4 hr wet oxidation.](image)

Figure 4-19 shows the TEM and Fast Fourier Transform (FFT) images of a nanobelt. The TEM image clearly shows the nanobelt is a single crystal. The d-
space measured from the FFT image is 0.1627 nm, corresponding to the (1120) planes of ZnO. This indicates that this nanobelt grows in the direction of [11\(\bar{2}0\)] and perpendicular to the C axis.

**Figure 4-20.** a) TEM image of a corner where the nanobelt growth changed direction. b) A high resolution image shows the growth direction at the corner. The nanobelt was formed at 420\(^\circ\)C after 4 hr wet oxidation.
More TEM study discovered that the growth direction of the nanowires/belts can change during the process of growth. However, the TEM image indicates that the nanobelt remained in a single crystal even when the growth direction was changed. The new direction is often in the same crystal direction class as the previous one. For example, the one in Figure 4-20, the angle between the two orientations is about 60 degrees, and all have about 30 degree angle with the [11\(-2\)0] directions. Therefore, it means that the nanobelt growth just changed from one <01\(-1\)10> class direction to another one.

Figure 4-21. HTTEM of the ZnO nanobelts crystal lattices. The nanowire was formed at 420°C after 4 hr wet oxidation.

Figure 4-21 is another HRTEM image showing that the growth direction can be [21\(-1\)0] as well, which is in the same direction class as [11\(-2\)0], also perpendicular to the C axis. Thus, the top/bottom surfaces of the nanobelt are still (0001)/ (000\(-1\)) and
the side surfaces are $\pm (0\bar{1}10)$, which are all stable faces. The growth direction perpendicular to C axis is different from the common behaviour in solution growth or most of the gas phase processes, where nanowires growth in the direction of [0002], which is parallel to C axis.

The reason causing this difference can be found from the growth mechanism at the initial stage, when the surface diffusion of Zn atoms and reaction with water vapour are dominant. It has been reported that the Zn diffusion rate is anisotropic. For Zn nanoparticles, its oxidation rate and evaporation rate in $<0\bar{1}10>$ directions are higher than that in $<0001>$ directions [181]. This gives evidences that Zn diffuse fast on the planes perpendicular to C axis. As comes to wet oxidation, this results in the nanobelt growing normal to (0002) direction.

4.3.2 CL Measurements

CL measurements were carried out on the ZnO nanowires as it is one of the widely used techniques to investigate local optoelectronic properties of nano-sized ZnO crystals because of its high spatial resolution [175-177]. Figure 4-22a is the investigated area for CL, and Figure 4-22b is the photo imaged by using the CL spectra from the sample. The nanowires are more obvious to see in the CL image, indicating that the light emission is mainly contributed by the ZnO nanowires, although the background is also ZnO.

The reason that ZnO nanowires exhibit stronger light emission may be due to that ZnO nanowires are single crystals and have better crystal quality and less defects than the bulk polycrystalline ZnO films. Since the light emission is mainly contributed from ZnO nanowires, the results of CL and PL spectra of the samples should mainly represent the characters of the nanowires, not the background. The
room temperature CL spectra of ZnO nanowires grown from Zn precursors are shown in Figure 4-23. The spectrum consist mainly of an UV peak centred at ~370 nm (~3.35 eV), with no obvious visible light emission. This result is consistent with the PL study.

Figure 4-22. a) SEM image of the CL investigated area, and b) The CL mapping of a). The sample was the 8-min Zn precursor after wet-oxidized for 2 hr at 420°C.
4.3.3 PL Measurements

Figure 4-24 illustrates the temperature dependent PL spectra of the ZnO nanowires synthesized by oxidizing the 8 min Zn precursor film for 4 hr at 420°C with an oxygen flow-rate of 0.3 LPM, (sample in Figure 4-7d). A sharp peak at the wavelength of at ~368 nm was observed at 10K, corresponding to the UV near-band edge emission. The ZnO nanowires synthesized by wet oxidation did not give any obvious visible light emission at the range of 510-700 nm [178], which is related to the deeper level defects such as oxygen vacancies and Zn interstitials. Therefore, the absence of visible light emission suggests that the ZnO nanowires synthesized by wet oxidation have a low density of defects. The peak intensities declined with increasing temperature due to more energy was transfer through thermal vibration.
The detail analysis of the temperature dependence PL spectra will be delivered with doped sample in the next chapter.

**Figure 4-24.** Temperature dependence PL spectra of ZnO nanowires from 10K to 280K. The sample was the 8-min Zn precursor after wet-oxidized for 4 hr at 420°C.

### 4.4 Summary

The correlation of deposition time and Zn precursor film structure was firstly studied to have a good understanding of the Zn precursor film growth process. The influence of the deposition current on the Zn structure was carried out. Then, the other influential factors, including Zn precursor structure, oxidation time, and oxidation temperature on the growth and morphology of ZnO have been examined and discussed. We found that almost all factors listed above have significant effects on the growth mechanisms and morphology of ZnO.

It was found that Zn precursors with deposition time of 5 to 9 min were more favourable for ZnO nanowires growth, and the optimum oxidation time and
temperature would be 4-5 hr, and at 420°C. Based on the study of above influential factors, the ZnO nanowire/belt growth mechanism during the wet oxidation was discussed, and was further proved by the study on the impact of oxygen flow-rate and water vapour variation.

HETEM study shows that the nanobelt grown from wet oxidation is single crystalline, and has the growth orientation perpendicular to the C axis. Together with the knowledge of the anisotropic diffusion behaviour of Zn, this TEM finding gives good support to the proposed growth mechanism. The TEM image also illustrates that when the nanobelt growth changed direction or a branch grew our of the existing structure, the single crystalline still retained.

CL mapping showed ZnO nanostructures have much stronger light emission than the background film, and both room temperature CL and temperature-dependence PL spectra produced similar results: the ZnO nanowires have strong UV peaks at ~370 nm with negligible visible light emission. This means that the nanowires have good crystal quality with low density of defects. The details of the time-dependence PL spectra will be further discussed together with the doped samples.
CHAPTER 5. SILVER DOPED ZINC OXIDE NANO-WIRES PREPARED BY WET OXIDATION

5.1 Introduction

Our recent work demonstrated that wet oxidation was a facile and efficient way for ZnO nanostructure synthesis. By controlling the processing parameters such as the initial surface morphology of Zn precursor, oxygen content, water vapour pressure, oxidation temperature and time, the desired single-crystal ZnO nanowire/belts with high density could be successfully fabricated. The ZnO growth mechanisms were discussed based on the experimental evidence of phase variation, micro-crystal structure and optical properties.

Currently, ZnO doping methods and processing parameters have attracted much attention since till now; there was still no reproducible doping method for stable \( p \)-type ZnO film and nanostructures, while the effective doping was absolutely essential for the ZnO based devices applications. Therefore, to judge whether or not wet oxidation is a promising technique for ZnO nanostructure synthesis, the doping ability, especially \( p \)-type doping ability, is an important consideration for investigation.

The wet oxidation is a two-step process, so doping can be made in either step, namely sputtering/deposition and wet oxidation steps. For doping in the first sputtering stage, it is important to note that the doping element should not change the Zn precursor structure too much. As demonstrated in previous chapter, the change in Zn precursor structure could strongly influence the formation of ZnO nanowires in the later oxidation stage. Therefore, to achieve \( p \)-type doping, Group-V elements such as N would be not suitable at this stage, as they will react with Zn,
and change its chemical states. The resulting film will not be metallic film. The chemical reaction will lead to major structure change of the initial precursors, and resultanty affect the final wet oxidation result.

Doping metallic elements in the sputtering stages is feasible. For $p$-type doping, Group-I elements and some transition metals are considered as the suitable candidates. However, Group-I elements are very reactive at their metal form. Thus, it is difficult and sometimes not safe to use them in our sputtering system for the doping. Furthermore, literatures have reported that the $p$-type conductivity resulted from Group-I doping were not good for ZnO due to that Group-I elements tend to go to the interstitial positions thus contribute to the $n$-type conductivity instead of $p$-type.

Amongst the transition metal elements, Ag is a candidate for potential $p$-type doping in ZnO, not only because it can act as an acceptor when substitute Zn site, but also due to its ability to enhance the ultra-violet (UV) emission of ZnO. For detailed reports please refer to the Section 5.2.2.

In this chapter, we firstly prepared the Ag doped ZnO (Ag:ZnO) films by magnetron sputtering (MS) method and investigate the roles of Ag dopant in ZnO film host. Then we focused more attention on the preparation of Ag:ZnO nanostructure fabrication by using wet oxidation technique. The effect of Ag doping on the final ZnO nanostructure fabrication as well as the doping effect on the optical properties were systematically investigated.

**5.2 Ag Doping in ZnO Thin Films**

Before conducting the Ag doping to ZnO nanostructure, the realization of $p$-type conduction by Ag-doping is conformed by examining the Ag:ZnO thin films. Ag:ZnO thin films were produced by MS, and annealed in different atmospheres
after the deposition. It has been found that with certain combination of the sputtering conditions and the annealing treatments, \( p \)-type conduction can be realized in some of the Ag:ZnO thin films. The results are briefly described in the following section.

5.2.1 Experimental Procedures

Two techniques were used to produce Ag:ZnO films with the MS system. The first one is reactive sputtering. Two 2 mm×35 mm Ag Stripes were attached to the Zn target surface. \( O_2 \) was introduced together with \( Ar \) during the deposition to perform reactive sputtering. The Zn and Ag atoms leaving the target, would react with \( O_2 \), and thus form Ag: ZnO films on substrate. The \( Ar : O_2 \) ratios of 5 : 5, 6 : 4 and 7 : 3 were used for the direct current (DC) reactive sputtering.

The second way is the normal DC sputtering, using ZnO as the target, and Ag strips were arranged in the same way as the first one. An \( Al_2O_3 \) buffer layer was also deposited before the ZnO deposition to improve the film crystal quality. \( Ar : O_2 \) ratio of 10 : 0 and 9 : 1 were used. The deposition time was fixed at 2 hr. Other experimental parameters were the same as mentioned in the previous chapter. Undoped ZnO films were also deposited using the same condition for comparison.

The as-deposited films were annealed in air, \( O_2 \) and \( N_2 \). Scanning electron microscopy (SEM), X-ray diffractometer (XRD), and Hall-Effect electrical measurement were used for the characterization.

5.2.2 Results

It was found four types of Ag-doped thin films were showing \( p \)-type conduction. Table 5-1 shows their deposition and post treatment conditions, as well as their electrical properties determined by Hall-Effect measurement system.
Table 5-1. The process parameters and electrical properties of selected Ag: ZnO films.

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<th>ZnAg2</th>
<th>ZnAg3</th>
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<tr>
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<td>6.04E+15</td>
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<td>p</td>
<td></td>
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From Table-5-1, it can be observed that all films exhibiting p-type conduction have one common point: they were all annealed in N2 atmosphere at 600°C for 4 hr. For films produced from reactive sputtering, when O2 percentage increased from 50% to 70%, the conductivity of the films changed from slightly p-type conduction to n-type conduction with high resistivity. This is probably because at low O2%, the film from reactive sputtering would have a large amount of oxygen vacancy (V_O), which is recognized as the native donor in ZnO. Thus, without annealing, this type film should exhibit n-type conduction. In fact, the films with the same deposition condition as ZnAg1-3, but without annealing, were too insulating to get any result from the Hall-Effect measurement, probably due to the bad crystal quality caused by Ag doping or due to the compensation effect.

However, when the samples were annealed in N2, the high concentration of V_O would give a high driving force for N2 diffusing into the ZnO crystal lattice. This is easier than the diffusion of N to perfect ZnO crystal, where one O atom has to
diffuse out to create a $V_O$ where an $N$ atom can diffuse to. Therefore, after $N_2$ annealing, the sample deposited with higher $O_2\%$ gave lower $p$-type conductivity.

$N$ may have contributed to the $p$-type conduction, but $Ag$ also played important roles for it, as the best $p$-type conductivity is measured from $ZnOAg-1$, which was deposited using $ZnO$-$Ag$ target. $ZnO$ film produced using $ZnO$ target with the same deposition parameters and also annealed in $N_2$ atmosphere for the same time and duration as $ZnOAg-1$ could not give $p$-type conduction. This proves the necessity of $Ag$ doping to deliver the $p$-type conduction.

The first result obtained from $Ag$ doping can be seen from the SEM and XRD analysis. Figure 5-1 shows the SEM image and XRD patterns of the three $p$-type conductive films, $ZnAg1$, $ZnAg2$ and $ZnOAg1$. The film with higher $p$-type conductivity has more obvious elongated-shape grains; and the XRD peak for (101) plane is more intense. The (101) peak could not observed from the un-doped $ZnO$ film deposited by MS. Therefore, the $Ag$ doping has changed the $ZnO$ film morphology and growth orientations, which could be a factor for the $p$-type conduction behaviour. There is no XRD peak related to $Ag$, indicating that $Ag$ doping did not form separate phases, but doped into $ZnO$ crystal lattice.

$Ag$ doping could also cause disruption of the $ZnO$ crystal lattice and create more $V_O$, which would favour $N$ diffusing to $ZnO$ host in the later annealing process. Moreover, in the as-deposited film, $Ag$ is amphoteric dopant, existing both on substitutional $Zn$ site and the interstitial sites. The annealing treatment would allow $Ag$ atoms to diffuse to the substitutional sites since this diffusion is more energy favourable. Thus, after heat treatment, both $N$ and $Ag$ act as acceptors when substituting $O$ and $Zn$ sites, respectively. As a result, the $p$-type conductivity of the film was greatly improved.
Figure 5-1. SEM images of samples showing p-type conductivity: a) ZnAg1, c) ZnAg2, e) ZnOAg1, and their corresponding XRD patterns: b), d) and f).

5.2.3 Conclusion

The above study on Ag:ZnO film shows Ag atoms can be a suitable candidate for ZnO film doping and can produce p-type ZnO films when combining with N₂ treatment. This gives the hint to develop Ag doping method for ZnO nanostructures using wet oxidation method.
5.3 Ag Doping for ZnO Nanostructures

Both literatures and our own experimental results have shown that the Ag doping can result in $p$-type ZnO. Therefore, it is feasible to extend the research on ZnO nanostructures.

5.3.1 Experimental Procedures

For MS deposition, the same setup and operation procedures were used as in the last chapter. The only difference is 2 silver strips were attached to the Zn target to achieve Ag doping to Zn precursor. Due to the limitation of them target configuration, the Ag doping cannot be accurately controlled. It can only be qualitative adjusted by changing the size of the Ag strips. The Ag doping level is roughly classified as low and high. The wet oxidation process was also the same as the last chapter, the oxidation time is 4 hr, and the temperature used was 420°C and 450°C. The water bath temperature was controlled at 45°C, and the oxygen flow-rate is 0.3 LPM. It is expected that some of the doped Ag atoms can diffuse into the ZnO nanostructures during the oxidation, and result in the Ag:ZnO nanostructures. The surface morphologies of the as-deposited precursor films and nanostructures formed after wet oxidation were characterized with SEM while their crystal structure was analyzed with XRD. The nanowire crystal structure was studied with a high resolution transmission electron microscopy HRTEM. The chemical state of the doping elements was analyzed by X-ray photoelectron spectroscopy (XPS) based on synchrotron radiation. Optical properties were measured by photoluminescence (PL) with a 325 nm laser source at low temperatures.

5.3.2 Results

5.3.2.1 Microstructures
Figure 5-2. The image of the precursor films: a) un-doped Zn, c) Ag-Zn with low doping level, e) Ag-Zn with high doping level, b), d) and f) are the ZnO structures formed after wet oxidation for films shown in a), c), and e), respectively.

Figure 5-2a shows that the typical un-doped Zn particles have a hexagonal-shaped and multi-layered structure with thin platelets. The study in last chapter has shown that this structure is favourable for ZnO nanowire formation. Figure 5-2b demonstrates that after the wet oxidation high density of ZnO nanowires were formed. From Figure 5-2c, it can be noted that the low level Ag-doped Zn (Ag-Zn) particles have relatively irregular shapes and large size variation, but small tips on the particle surface were still retained.
The nanowires were formed during wet oxidation as shown in Figure 5-2d. However, the density of the nanowires is much lower than that shown in Figure 5-2b. If further increased the Ag doping level, it would change the precursor film dramatically as shown in Figure 5-2e. Small and irregular shape particles were formed, and after wet oxidation, no nanostructure can be produced. These observations suggest that the presence of Ag depressed the growth of ZnO nanostructures. Ag doping level needs to be restricted at a relatively low level to ensure the growth of ZnO nanostructures.

Research on Sn-Ag-Zn based soldering alloy suggested that Zn and Ag could form metallic compounds solution above 300°C, which would inhibit the Zn oxidation [182]. It may be one of the reasons that as the doping level of Ag increased, the ZnO nanowire growth was discouraged. The doped Ag atoms may also block the diffusion path for Zn, which is important at the initial stage of the nanowires growth, as discussed in last chapter. This could be the other cause of reduction of the ZnO nanowire growth.

5.3.2.2 TEM Analysis

Thermodynamically, Ag could not exist in oxide form at a temperature above ~100°C. But at elevated temperature, Ag should be able to diffuse though the ZnO lattice. Due to the different diffusion rates and oxidation behaviour of Zn and Ag, the concentration of Ag at the root of the nanobelts should be the highest and then gradually decreased along the direction to the tip. TEM observation confirmed this assumption clearly and directly.
Figure 5-3. TEM image a) IFFT images from the root of an Ag:ZnO nanobelt, b) and c) the IFFT and HRTEM images of the middle section of the same Ag:ZnO nanobelt.
Figure 5-3a shows one of the Ag:ZnO nanobelt to be examined. HTTEM images were taken at the root and middle section of the nanobelt as indicated by the white frame in Figure 5-3a, and the images are shown in Figure 5-3b & 3c. Figure 5-3d & 3e are the inverse fast Fourier transformed (IFFT) image of Figure 5-3b & 3c, respectively, and the transformations were made by the software Digital Micrograph.

Figure 5-3b & 3c indicate that the nanobelt growth direction did not change from the root to middle section, and the growth direction is [2 1 1 0], the same direction as the un-doped ZnO nanobelt shown in the last chapter (Figure 4-20). Distorted crystal lattices can be observed at the root of the nanobelts. The dislocations are clearly seen in the IFFT image (Figure 5-3e), and have highlighted by the yellow frames. The large amount of dislocations and defects could be caused by Ag doping, as the Ag ionic radius (0.115 nm for Ag\(^+\), and 0.094 nm for Ag\(^{2+}\)) is much larger than that of Zn ion (0.074 nm for Zn\(^{2+}\)).

The HRTEM and IFFT images of the middle section of the belt are shown in Figure 5-3c & 3d, which shows an almost perfect single crystal structure with no dislocation, indicating the absence of Ag atoms in ZnO crystal. These observations confirmed the hypothesis that the Ag dopants were not distributed in the nanowire/belts uniformly and there is a concentration gradient along the bottom to top of each nanowire/belt.

### 5.3.2.3 XPS Results

Figure 5-4 illustrates the Ag 3d XPS spectra based on synchrotron radiation from the Ag:ZnO nanowire with the low doping level, and the result has been calibrated according to Carbon 1s peak at ~285 eV [183]. Ag with a low concentration cannot be clearly detected by normal laboratory XPS system. The XPS result shows that the 3d\(_{5/2}\) peak of Ag from the Ag:ZnO sample is located at 367.5 eV, and the 3d\(_{5/2}\) peak
for pure metallic Ag is at 368.2 eV [184]. Therefore, this result indicated that the doped Ag existed in ZnO matrix as Ag ions rather than elemental metallic Ag.

\[ \text{Figure 5-4. Ag 3d peaks for Ag:ZnO nanowires with low doping level and the exciting photon energy is 600 eV.} \]

The 3d\textsubscript{5/2} peak can be attributed to the Ag-O bond in Ag\textsubscript{2}O. However, the binding energy (B.E.) values shifted from the standard position to the lower values for 0.2 eV (standard B.E of Ag 3d\textsubscript{5/2} in Ag\textsubscript{2}O is 367.7 eV [185]). This could be because that firstly, the Ag existed in ZnO matrix interacted with Zn and O, thus its chemical state was not the same as its pure oxides (Ag\textsubscript{2}O, AgO). Secondly, Ag was doped into the ZnO nanowires, and the low dimension induced larger surface of nanowires might also cause the difference due to the surface bonding effect [186]. Nevertheless, the XPS results prove the existence of Ag\textsuperscript{+} in the Ag-ZnO nanowire. If the Ag\textsuperscript{+} ions are in the Zn site, they can act as acceptors to deliver p-type conduction.
Figure 5-5. a) Ag 3d peaks for Ag:ZnO nanowires with high Ag-doping level, and the exciting photon energy is 600 eV. b) Ag 3d$_{5/2}$ peak fitted numerically with the mixed Gaussian-Lorentzian functions.

The Ag chemical states of the Ag:ZnO film with high doping level was also checked. Figure 5-5a shows its Ag 3d peaks. It can be seen that with high Ag doping
concentration, the Ag 3d peaks become much sharper and stronger. The 3d$_{5/2}$ peak was fitted numerically with the mixed Gaussian-Lorentzian functions after background subtraction, shown in Figure 5-5b. The fitting curves illustrate that the 3d$_{5/2}$ peak can be spited into two peaks located at 367.5 eV and 367.2 eV. The strong peak at 367.2 eV should be attributed to the Ag-O binding in AgO, but also shifted for 0.2 eV (standard B.E of Ag 3d$_{5/2}$ peak in AgO 367.4 eV [187]). The reason of the shifting should be similar to the previous one, only without the effect from the nanostructures.

It should be noted that with high level of Ag doping, the Ag 3d$_{5/2}$ peak at 367.2 eV become dominant. This suggests that the additional Ag would tend to exist in the form of Ag$^{2+}$. The reason of this is unclear, but Ag can only acts as acceptor when it is in the form of Ag$^+$, so the addition of Ag is not helpful for the $p$-type conduction, and the microstructure studies have also shown that with high doping level ZnO nanostructures could not grown up. Therefore, it can be concluded that Ag doping at the low level is favourable to both ZnO nanowire growth and electrical properties.

5.3.2.4 PL Properties

Figure 5-6 illustrates the 10K PL spectra of the Ag:ZnO and pure ZnO nanowires. It is noticed that as same as the pure ZnO nanowires, Ag:ZnO nanowires synthesized by wet oxidation do not give any obvious visible light emission at the range of 510-700 nm, which is related to the deeper level defects such as O vacancies and Zn interstitials. Therefore, the absence of visible light emission suggests that the Ag:ZnO nanowires synthesized by wet oxidation also have a low defect density.

The light emission of Ag:ZnO in the UV region is significantly stronger than that of pure ZnO, with the intensity of almost three times higher. The enhancement
of UV emission is a character of Ag doping, which has been reported by Fu’s group [93, 144]. It is believed that this enhancement is due to that the photo-carrier may escape more easily from Ag ions than from Zn ions. This leads to the quick diffusion of exciton in ZnO and increased the exciton concentration, thus increasing excitonic recombination and resulting in stronger UV emission [144]. The insert in Figure 5-6 shows more details of the PL spectrum at UV region. The acceptor exciton (A^0X) peak became dominant over donor exciton (D^0X) peak in Ag:ZnO, which could be resulted from the Ag doping.

Figure 5-6. The PL spectra of pure and Ag:ZnO nanowires at 10K.

Figure 5-7 shows the temperature dependent PL spectra of ZnO and Ag:ZnO from 10K to 100K, and plots of the peak intensity changes as a function of temperature. The temperature dependent PL measurements show that the UV peak intensities of Ag:ZnO and pure ZnO do not always decrease with increasing
temperature. For pure ZnO, the total UV peak intensity decreases gradually from 10 to 50K, then rises again from 50 to 80K.
Figure 5-7. Temperature dependent PL spectra: a) Pure ZnO nanowires from 10K to 100K, b) Ag:ZnO nanowires from 10K to 280K, with 10K to 100K detailed shown in a small window. The peak intensities versus temperature from 10 to 100K: c) pure ZnO nanowires, and d) Ag:ZnO nanowires.
For a more detailed description, the relative intensity of D\(^0\)X peak is slightly stronger than that of A\(^0\)X from 10 to 30K (Figure 5-7a). The A\(^0\)X peak gets stronger than D\(^0\)X peak starting from 40K and has slight red shift. At 80K, D\(^0\)X and A\(^0\)X merge to form one peak at the position between D\(^0\)X and A\(^0\)X. With the temperature increasing up to 100K, the D\(^0\)X emission is almost disappeared due to thermal quenching, and the intensity of total UV emission drops again (Figure 5-7a). The temperature dependent intensity of D\(^0\)X and A\(^0\)X peaks indicates that A\(^0\)X emission in pure ZnO nanowire is more thermally stable than D\(^0\)X, although the D\(^0\)X peak seems stronger at a lower temperature such as 10K.

For the Ag:ZnO sample, the UV peak intensity changes generally in the same way as the pure ZnO, but the valley appears at 40K instead of 50K as for pure ZnO nanowire. Both D\(^0\)X and A\(^0\)X peak values augment after 40K, and reach another maximum point at 60K, as shown from Figure 5-7d, and then drop again. This peak intensities rise from 40K to 60K is more obvious than that of pure ZnO. The other distinction is that the A\(^0\)X peak of Ag:ZnO is stronger than D\(^0\)X peak from 10K to 80K, which is opposite to the pure ZnO. Only after temperature rises to 100K, the A\(^0\)X peak becomes slightly weaker than D\(^0\)X.

5.3.3 Discussions

Generally, PL peak intensity is directly related to the exciton concentration and the possibility of radiative transition, which are both associated with temperature. Normally PL peaks of semiconductor materials always decrease with increasing temperature due to the non-radiative transition process that a part of energy in the combination process of electrons and holes is consumed by lattice vibration. However, the exciton concentration is also associated with the temperature since
thermal energy is required for the ionization of donors or acceptors follow the relation:

$$n = (n_0N_d)^{1/2}\exp(-E_d/2k_BT)$$ \hfill 5- 1

$$n_0 = 2(m_ek_BT/2\pi\hbar^2)^{3/2}$$ \hfill 5- 2

where $N_d$ is the concentration of donor, $E_d$ is the ionization energy of donor and $T$ is the absolute temperature [112, 188]. The similar relationship also works for acceptor.

Accordingly, at extreme low temperature level such as 10K, the donor/acceptor will not be fully ionized, thus the effective concentration of exciton is relatively low. As the temperature increases to a certain level (60K for pure ZnO in this case), all of the donors or accepters are ionized, and the hole concentration on accepter band and the electron concentration on donor band are increased. So it is clear that there is a competition between the non-radiative transition process and the concentration of exciton, which are both associated with temperature. At a very low temperature, the increase in concentration will lead to a higher electron-hole recombination rate, and this effect can be more significant than the thermal vibration effect on the reduction of light emission. This should result in an increase in light emission intensity. If temperature keeps increasing to a point where all or most of the donor and acceptor are ionized, further increasing temperature will not give much more concentration increase of electron-hole, and then the thermal vibration induced non-radiative effect dominates again. From the experiment result, this turning point for pure ZnO is at 80K and for the Ag:ZnO is 60K.

This mechanism gives a reasonable explanation for the different character for ZnO and Ag:ZnO. For ZnO, at 10K D$^0$X emission is more dominant over A$^0$X, suggesting pure ZnO is native $n$-type semiconductor. In the first decreasing region
of 10K to 50K, the intensity reduction rate over temperature of D^0X is greater than that of A^0X, so that at 50K, the A^0X emission is more intensive than D^0X. This suggests that the thermal vibration effect has more impact on the D^0X emission than on A^0X. After temperature rise above 50K, donors and accepters start to be ionized, and as in pure ZnO, donor is more dominant, therefore, ionized donor concentration should be larger than accepter. Thus at 60K, D^0X peak become higher than A^0X again, and both D^0X and A^0X peak are red shifted from the original position. At 80K, the ionized donor and acceptor concentrations get saturated, thus the intensity reaches another maximum point. After that, thermal vibration effect take over the place again. As the D^0X emission is mainly influenced by the thermal vibration, it decreases dramatically when temperature increases to 100K, at which temperature almost only A^0X left.

Regarding to Ag:ZnO, A^0X is stronger than D^0X from 10K up to 80K, indicating that the Ag doping enhanced the A^0X emission as Ag acts as acceptor when substituting Zn site. But the Ag acceptor site is easy to be influenced by temperature. Therefore, at 100K and above the A^0X peak become weaker than D^0X. The turning point of first decline region to increasing region for Ag:ZnO is at 40K, 10K lower than pure ZnO. This should be due to the fact that Ag is easier to be ionized than the native acceptor in pure ZnO, so the ionized acceptors start to appear at lower temperature in Ag:ZnO. The Ag doping on the ZnO structure may also have an effect on donor site (H_i, V_o). As a result, lower energy is required to ionize them, so the turning point for D^0X decreased to 40K too.

5.4 Summary

The realization of p-type conductive ZnO by Ag-doping has been demonstrated possible on MS deposited ZnO films. The Ag:ZnO film can exhibit p-type
conduction with resistivity at \( \sim 10^2 \ \Omega \text{cm} \) level if annealed in \( N_2 \). Ag:ZnO nanowires have been synthesized by using the wet-oxidation process. It was observed that Ag doping has hindered the growth of nanowires, reducing their population density. The HRTEM observation gives an evidence of the Ag existence in the ZnO nanowires. XPS indicates that the doped Ag is in oxide chemical state in ZnO.

The study of PL results shows that Ag doping enhanced the ZnO nanowires UV emission by more than three times. This could be attributed to the photo-carrier escape more easily from Ag ions than from Zn ions. For pure ZnO nanowires, \( D^0 \lt X \) emission is dominant over \( A^0 \lt X \), consistent with the natural \( n \)-type ZnO conductivity. However, \( D^0 \lt X \) emission is more temperature sensitive than \( A^0 \lt X \) in pure ZnO nanowires. For Ag:ZnO nanowires, doped Ag acts as acceptors, and reduce the ionization energy of acceptors in ZnO and thus enhanced \( A^0 \lt X \) emission. However, due to the facility limitation, the electrical properties of the Ag:ZnO nanowires cannot be directly measured, which is a weakness of this research. I would like to pursue possible assess to the facilities that can give reliable direct electrical properties of the Ag:ZnO nanowires.
CHAPTER 6. NITROGEN DOPING TO ZINC OXIDE NANOWIRES WITH WET OXIDATION PROCESS

6.1 Introduction

As mentioned in the last chapter, each step of the wet oxidation process can be utilized to conduct doping. The first step of sputtering is suitable for metal elements substituting Zn, and the second step of wet oxidation should be able to deliver doping of gas elements for substituting O. N is the most intensively studied element as the $p$-type dopants for ZnO. Some works related to N doping have been introduced in Section 2.3.5.2. The studies shown in the last chapter also indicate that the combination of Ag and N doping can produce good $p$-type conduction for ZnO films. Therefore, it is reasonable to explore the method that can produce N doped ZnO (N:ZnO) nanowires with the wet oxidation technique.

NH$_3$ has been used as the source chemical to conduct N doping to ZnO by many researchers [81, 85]. It is also reported that Zn powder can react with NH$_3$ to form Zn$_3$N$_2$ nanowires at 600°C [189]. NH$_3$ is a volatile chemical and soluble to water. Therefore, if replacing the deionised (DI) water in the water flask with NH$_3$ solution, with the O$_2$ bubbling through the solution before it flows into the furnace, it is expected that, the Zn precursor can react with NH$_3$ during the wet oxidation process, and thus introduces N into the ZnO matrix, resulting N doping.

This chapter describes the doping process and studies the effectiveness of N doping. The Ag doped Zn (Ag-Zn) precursor was also used to further investigate the effects of the combined Ag and N doping.
6.2 Experimental Procedures

The Zn and Ag-Zn precursor films were prepared with the same conditions as described in the last chapter. The precursors were oxidized in a tube furnace at 450°C and 600°C with an O₂ flow-rate of 0.3 LPM for 4 hr. The dry O₂ was bubbled through a water flask containing NH₃ solution (3.5%) before flowing into the furnace, so that the O₂ could carry water and NH₃ into the furnace to conduct wet-oxidation and N doping at the same time. The water flask was kept in a water bath with controlled temperature. The amount of water vapour content carried to the furnace was controlled by the water bath temperature. 45°C was used for all the experiments in this research. At 45°C, for 3.5 wt.% NH₃ solution, the water vapour pressure was 9330 Pa and the NH₃ vapour pressure was 11625 Pa [190]. Therefore the mole fraction of water and NH₃ in air is 9.21% and 11.47 %, respectively, according to Equation 3-1.

The exhausted gas was flowing though three flasks in series containing diluted HCl solution to absorb the residual NH₃. A portion of the samples oxidized at 450°C were also annealed in N₂ at 600°C for 1 hr. The characterization methods were the same as those used in the last chapter, including scanning electron microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS), and Photoluminescence (PL) measurements.

6.3 Results

6.3.1 Microstructures

The SEM study investigated the surface morphologies of the Zn and Ag-Zn precursor films after wet oxidation. After oxidized in H₂O/NH₃/O₂ atmosphere at 450°C for 4 hr, ZnO nanowires with the length of several microns formed on the surface of the sample (Figure 6-1a). Compared with the specimens oxidized without
NH\textsubscript{3} at the same condition, the length and diameter of the nanowires treated in the mixed atmosphere are reduced, and the population density is lower too. If the oxidation temperature increased to 600\textdegree C, the density of the nanowire is further reduced (Figure 6-1b).

For the Ag-Zn precursor, it is interesting to find that the nanowires with greater length and density formed after H\textsubscript{2}O/NH\textsubscript{3}/O\textsubscript{2} treatment at 450\textdegree C (Figure 6-1c),
which is opposite to our previous study, where with H$_2$O/O$_2$ treatment Ag-Zn yielded fewer nanowires than pure Zn at this temperature range. When the temperature increased to 600°C, nanowire growth is inhibited, which followed the same trend as the un-doped Zn, and the extent of inhibition is even higher than the un-doped Zn (Figure 6-1d).

The introduction of NH$_3$ to the wet oxidation process inhibited the nanowire growth from Zn precursor can be attributed to the reduction of O$_2$. In our previous experiment when bubbling O$_2$ through DI water at 45°C, the water vapour concentration was 9.5% and O$_2$ concentration was 90.5%. After replacing the DI water with 3.5% NH$_3$ solution, NH$_3$ had higher vapour pressure than water at this temperature, and it was accounted for 11.5% in the gas phase, while H$_2$O% was maintained at the same level (9.2%). Therefore the O$_2$ concentration was reduced to 79.3%, more than 10% lower than before. Thus, at the same oxidation temperature, lower O$_2$ concentration may result in the reduced growth of nanowires.

It is interesting to note that the Ag-Zn precursor grew nanowire even better than Zn precursor in NH$_3$/H$_2$O/O$_2$ atmosphere, and also better than Ag-Zn in H$_2$O/O$_2$. The previous study has demonstrated that the Ag-Zn precursor did not grow well in wet oxidation process. This could be due to the formation of Zn-Ag intermetallic compounds above 300°C which affected the oxidation process of Zn [182], and thus Ag-Zn did not grow good nanowires in O$_2$/H$_2$O. With NH$_3$ present, Ag may play a catalyst role for NH$_3$ dehydrogenation, similar as Ir, Pt and Ni reported by other researchers [191, 192]. It may have promoted the reaction between Zn and NH$_3$. Thus in the NH$_3$/H$_2$O/O$_2$ atmosphere, nanowires grew better from Ag-Zn precursors. However, annealing in N$_2$ at 600°C damaged the nanowire structures for both undoped and Ag-Zn samples, shown in Figures 6-1e and 6-1f.
6.3.2 TEM Study

Figure 6-2. TEM images of Ag-N:ZnO nanowires formed after wet oxidation at 450°C.
TEM study observed some interesting microstructures from Ag-N co-doped ZnO (Ag-N:ZnO) nanowires. It can be seen that there are many black spot distributed in the nanowires (Figure 6-2a). The density of these black spots seems decreases from one edge of the nanowires to the other edge. A close look under high resolution TEM (HRTEM) shows the nanowire is crystalline ZnO. The lattice spacing of 0.28 nm labelled on the Figure 6-2b is corresponding to the $[2\overline{1}10]$ plane of ZnO. The nanowire growth orientation is the same as the ZnO and Ag:ZnO nanowires, as shown in Chapters 4 and 5.

There is an amorphous region on the edge of nanowire. The dark spots can be found at both the crystalline and amorphous regions. However, at the crystalline region, the dark area has the same crystalline structure as the rest area; different phase can not be seen. At the amorphous region, the black area is more obvious to be observed, which is easier to be identified at the low magnification image (Figure 6-2a). It seems that the black spots formed on one of the edge first and crystallized into the crystal lattice.

Figure 6-3a shows a branch grown out from the nanowires. It also has the black spot at the tip. A similar distribution of the black spots can be observed from the branch. There are more black dots on the left side of the branch, and disappear on the right side. Figure 6-3b displays more details at the junction area of this branch. The upper part has a clear crystalline structure with periodic crystal lattice, while the area at the lower left corner looks amorphous. The lattice spacing at the crystalline region is measure to be 0.28 nm in Figure 6-3c, same as the one in Figure 6-2b.
Figure 6-3. TEM images taken at a branch of a Ag-N:ZnO nanowire.

Figure 6-4 shows the HRTEM images of the amorphous regions at high magnification. It demonstrates that each of the black spot is a single crystal grain. These small grains are randomly packed in the amorphous matrix. The matrix and the small grains tend to crystallize and become single crystals as shown in Figure 6-4d, where the long periodic crystal structure has formed.

From Figure 6-4, it can be noted that the crystal lattice of the small grains looks clear on the edges of the material, and become vague when moved away from the edge. The lattice spacing of the grains on the edges (circled by yellow dash lines)
was measured, and the values are all about 0.217-0.218 nm, which is corresponding to [420] plane of Zn$_3$N$_2$. The lattice structure away from the edge becomes less distinct, and the measured lattice spacing becomes larger. The increase in lattice spacing can even be observed in a single grain, which is circled by blue dash line in Figure 6-4b. The decrease in crystallinity of Zn$_3$N$_2$ and increase of lattice spacing should be resulted from the transformation of Zn$_3$N$_2$ to ZnO. Figure 6-4d shows the result after the transformation, the measured lattice spacing is 0.28 nm, which proves the crystal structure is ZnO.

![Figure 6-4](image.png)

*Figure 6-4. The amorphous part of the Ag-N: ZnO nanowire; the parts circled with yellow dash line are Zn$_3$N$_2$."

However, there are still many dislocations and defects in the crystal structure, suggesting that the crystallization is not fully completed. This TEM results demonstrated the formation of Zn$_3$N$_2$ and its conversion to ZnO. The TEM image of
the nanowires formed from Zn precursor in the O₂/NH₃/H₂O do not show the same phenomenon, which suggest that the formation of a large amount of Zn₃N₃ is related to the existence of Ag.

### 6.3.3 XPS Results

**Figure 6-5.** XPS N1s spectra: a) N:ZnO, and b) Ag-N:ZnO. Black square: wet oxidation in NH₃/H₂O/O₂ atmosphere at 450°C for 4 hr, red dot: wet oxidation in NH₃/H₂O/O₂ atmosphere at 450°C for 4 hr and annealed in N₂ for 1 hr at 600°C, and green triangle: wet oxidation in NH₃/H₂O/O₂ atmosphere at 600°C for 4 hr.
In order to investigate the chemical states of the N doping in the ZnO nanowires, photoelectron spectroscopy (PES) experiments based on synchrotron radiation were conducted. The N1s core-level spectra for different samples are shown in Figure 6-5a. The binding energy is calibrated using the C1s peak (285 eV). The N 1s peaks obtained with synchrotron radiation are much clearer than those obtained by the laboratory based XPS due to not only the high photon flux, but also the enhanced excitation cross section of N 1s electrons with exciting photons of 600 eV.

For the ZnO nanowires grown in H2O/NH3/O2 atmosphere at 450°C, the main peak is located at 398.8 eV (peak A) and another two peaks are at 398 eV (peak B) and 399.8 eV (peak C), shown in Figure 6-5a. Peak A is attributed to the substitution of N molecules at O sites in ZnO, (N2)O [87], and peak B is corresponding to the N bound to zinc (Zn-N) [193], while peak C is from N-H bond [194]. This result suggests that after react with NH3/H2O/O2 at 450°C, some N had incorporated into the ZnO lattice, but the majority of N formed N2 eventually, probably due to thermal diffusion.

Samples annealed at 600°C in N2 gave similar XPS spectrum. Only see that the peak related to N-Zn is reduced, indicating more N atoms formed N2 by diffusion during the annealing. This result is consistent with the finding reported in the literature about the formation of N:ZnO by oxidizing Zn3N2 [87].

When the wet oxidation take place at 600°C, peak C at 399.8 eV becomes stronger and peak A is depressed, another peak at 403.7 eV emerged, corresponding to the N-O bond [87]. This suggests that at 600°C the reaction between NH3 and O2 became significant, and therefore compete with the reaction between NH3 and Zn. Moreover, at 600°C, N atoms in ZnO lattice are easier to diffuse together and form N2, which would either occupy the O sites to form (N2)O or escape out of the crystal
Chapter 6. N doping to ZnO Nanowires with Wet Oxidation Process

lattices. These are the reasons that the intensities of the peak A and peak B were reduced.

The N-H bond is considered to come from the residual H from decomposed NH3. The reason for its corresponding peak (peak C) being intensified after 600°C annealing is not entirely clear, but from microstructure studies, some hints can be see. The SEM images show that after annealing treatment at 600°C, very few of nanowires formed since most of the Zn has been oxidized in the bulk form. Thus the N-H could be more favourable to form in the bulk ZnO.

For the Ag-Zn, the main peak of N1s appeared at 398 eV with a shoulder at 399.1 eV after 450°C annealing treatment. This means that a large amount of N has bonded to Zn directly. This is consistent with the TEM observation of Zn3N2 small grains in the ZnO nanowires.

After an annealing in N2 at 600°C for 1 hr, a peak at 398.7 eV appeared, corresponding to (N2)O. (N2)O could come from either the diffusion of N atoms in ZnO lattice to form N2, or the diffusion of N2 from the annealing atmosphere.

Samples from annealing at 600°C in NH3/H2O/O2 gave a similar XPS spectrum as the un-doped Zn, suggesting that the reaction behaviour of Ag-Zn at 600°C is similar to the un-doped one. The peak at 399.1 eV could still be attributed to the N-H bonding. The slight shift of binding energy may be caused by the effect of silver dopants. Evidently the current XPS study demonstrates that the Ag doping does not only favour the ZnO nanowire growth but also stabilized the N-Zn species in ZnO.

6.3.4 PL Properties

The PL spectra of the pure ZnO, N:ZnO and Ag-N:ZnO nanowires synthesized at 450°C were measured at 10K with various excitation energy. Figure 6-6 illustrates the low temperature (10K) PL spectra with full excitation energy. PL measurement
is a suitable tool to determine the crystal quality and the presence of defects/impurities in ZnO materials. Normally, the PL spectrum of ZnO consists of a sharp UV emission and broad emission in visible light region. UV emission is attributed to the excitation recombination, and the origin of visible broadband is related to the structural defects and/or impurities.

For all testing samples, PL spectra show a strong UV emission at ~369 nm, while N:ZnO also give obvious green emission start from 500 nm. In contrast, the green emission of pure ZnO nanowire is very weak, although still visible. For Ag-N:ZnO, no visible light emission can be detected. It can be noted that the UV emission of Ag-N:ZnO nanowires is much higher than the pure ZnO and N:ZnO samples, while the emission from N:ZnO is the weakest among the three. Therefore, the enhanced UV emission of Ag-N:ZnO should be resulted from Ag, which is consistent with the work shown in the last chapter.

![Figure 6-6. PL spectra of ZnO, N:ZnO and Ag-N:ZnO at 10K. The insert graph shows more details at the UV region.](image)
It is obvious that Ag-N:ZnO UV emission consists of 2 peaks, located at 368.1 nm and 368.9 nm, respectively. The pure ZnO have the similar character; only that the peak at 369 nm is not as strong as from Ag-N:ZnO. However for N:ZnO, the peak at 368 nm is not observable but another shoulder at around 370 nm can be seen, which should be result from N doping. Other researcher has reported similar results [195].

Excitation intensity dependent PL spectra study was also carried out to characterize whether the UV emission originated from the excitonic, donor-accepter pair, or free-to-bound like transition [144]. Generally the luminescence intensity varies with the excitation power as:

\[ I = \beta P^\alpha \]  

Where \( I \) is the PL intensity, \( \beta \) is a constant, \( P \) is the excitation power, and \( \alpha \) is an exponent. For the excitation energy exceeding the band gap energy, \( \alpha \) is between 1 and 2 for the excitonic like transition, and \( \alpha < 1 \) for free-to-bound and donor-acceptor pair transitions.

Figure 6-7b shows the intensity dependent PL spectra of ZnO, Ag-N:ZnO and N:ZnO measured at 10K. Figure 6-7a is the log-log plot of PL intensity as a function of the excitation power from ZnO, N:ZnO and Ag-N:ZnO nanowires. The intensities of UV emission of PL spectra under various excitation powers can be fitted by the power law. It is found that the slopes are \( \alpha = 1.47, 1.27 \) and 1.61 for ZnO, N:ZnO and Ag-N:ZnO nanowires, respectively, exhibiting a reasonably good linear behaviour. This suggests that the UV emissions from ZnO, N:ZnO and Ag-N:ZnO nanowires are of an excitonic origin, and the N or Ag doping does not alter the luminescence mechanism.
Figure 6-7. a) The log-log plot of PL intensity as a function of excitation energy, and b) intensity dependent PL for ZnO, Ag-N:ZnO and N ZnO at 10K.
6.4 Discussions

The TEM and XPS studies have demonstrated the existence of Zn$_3$N$_2$ in the nanowires formed from Ag-Zn precursor after O$_2$/H$_2$O/NH$_3$ treatment at 450°C. The TEM image also shows the transformation of the Zn$_3$N$_2$ to single crystal ZnO. The Zn$_3$N$_2$ should come from the reaction 6-2:

$$3Zn + 2NH_3 \rightarrow Zn_3N_2 + 3H_3$$  \hspace{1cm} 6- 2

As reported that this reaction starts to take place with a relatively high rate at a temperature over 600°C. This is why the oxidation temperatures used in this chapter are 450°C and 600°C. The results have shown that the oxidation at 600°C did not yield much ZnO nanowires, and Zn$_3$N$_2$ could not be observed from ZnO nanowires grown from Zn precursors oxidized at 450°C due to the low reaction temperature.

However, Zn$_3$N$_2$ can be observed in the ZnO nanowire formed at 450°C oxidation from Ag-Zn precursors. Ag has been studied as dehydrogenation catalysis for a long time [196, 197]. Although it has lower dehydrogenation capacity for NH$_3$ compared to Ru and Pt [198], it can still assist the decomposition of NH$_3$ to certain extent. Therefore, the presence of Ag should have reduced the Zn-NH$_3$ reaction temperature, resulting in the formation of Zn$_3$N$_2$ at 450°C.

The synthesis of N:ZnO by thermal oxidation of Zn$_3$N$_2$ has already been reported by some researchers [157-159, 194]. As Zou et al demonstrated, the Zn$_3$N$_2$ would start to transform to ZnO at 400°C, and an oxidation treatment at 450°C for 2 hr would have most Zn$_3$N$_2$ transferred to ZnO. Therefore Zn$_3$N$_2$ formed from reaction 6-2 is not stable at 450°C in the oxygen rich atmosphere. Soon after the Zn$_3$N$_2$ nanocrystals formed, they were oxidized to ZnO and recrystallized to the ZnO nanowire crystal structure.

As the formation of Zn$_3$N$_2$ and its transformation to ZnO are continuous processes, there were still Zn$_3$N$_2$ left at the end of the oxidation, so this
transformation process can be observed by TEM shown in Figure 6-4. As demonstrated by the reports on oxidation of Zn$_3$N$_2$, even after the transformation to ZnO, there could be still a significant amount of N remain at the O sites, and inducing $p$-type conduction. A parallel study in our group on oxidation of Zn$_3$N$_2$ film has produced $p$-type ZnO films following the same principle. The same fact should be held for the Ag-N:ZnO nanowires discussed above. This should be able to confirm by the direct electrical measurement on the single nanowires.

6.5 Summary

N:ZnO nanowires have been synthesized by using wet-oxidation process. High-quantity nanowires can be produce at 450°C but not at 600°C. However introducing of NH$_3$ to the oxidation atmosphere has hindered the growth of nanowires at 450°C for pure Zn precursor film; and XPS study indicated that at this temperature N has already incorporated into ZnO lattice, and mainly in the form of (N$_2$)$_3$ form.

Ag doping prior to the oxidation process can assist the growth of ZnO nanowires in NH$_3$/O$_2$/H$_2$O, and both length and the density of the nanowires have increased from the Ag-Zn after the oxidation treatment at 450°C. Zn$_3$N$_2$ nanocrystals can be identified in the Ag-N: ZnO nanowires by TEM, and XPS demonstrated that Ag-Zn has higher Zn-N concentration after 450°C oxidation treatment, inferring that Ag assisted the reaction of Zn with NH$_3$ at 450°C. This is important for achieving p-type ZnO by nitrogen doping.

The PL spectrum of the N:ZnO has the peak which can be assigned to the acceptor state comes from N doping according to the report published by other researchers. This process showed an evidence of N doping as accepter. However, this needs to be further confirmed by direct electrical conductivity measurement.
CHAPTER 7. SYNTHESIS OF ZINC OXIDE AND ZINC OXIDE/ TITANIUM DIOXIDE POROUS FILMS BY WET OXIDATION PROCESS

7.1 Introduction

The previous three chapters have shown that wet oxidation is a promising technique to produce ZnO nanowires/belts. Doping has also been achieved through various ways with wet oxidation to alter or tune the properties of ZnO nanostructures. In this chapter, the extended study of wet oxidation technique to produce ZnO and ZnO/TiO$_2$ composite porous films is described. The background information about TiO$_2$, porous film and photocatalysis in additional to Chapter 2, is given in the following sections.

7.1.1 Titanium Dioxide (TiO$_2$)

TiO$_2$ normally exists in three states in ambient conditions: anatase (tetragonal), brookite (orthorhombic), and rutile (tetragonal) [199]. The first two phases can transform to rutile upon heating. Similar to ZnO, TiO$_2$ also has a large band-gap energy of 3.2 eV [200] for anatase phase and 3.0 for rutile phase [201]. In 1972, Fujishima and Honda discovered the photocatalytic splitting of water on TiO$_2$ electrodes, which is now known as the Honda-Fujishima effect [202]. Since then extensive efforts in enhancing the photocatalytic efficiency of TiO$_2$ have come from research performed by scientists and engineers. Most of these studies are related to energy renewal and energy storages [203].

In the mid 1990s, the light-induced amphiphilic properties of TiO$_2$ were discovered. Combining this with the photocatalytic ability for total destruction of organic compounds and chemical stability in various environmental conditions, TiO$_2$
has been actively studied for the applications of environmental cleanup in polluted air and wastewater. Some of the research achievements have been commercialized, such as the TiO$_2$ coated self-cleaning glass and anti-fog mirror. Figure 7-1 illustrates the amphiphilic properties of TiO$_2$.

Figure 7-1. a, A hydrophobic surface before ultraviolet (UV) irradiation. b, A highly hydrophilic surface after UV irradiation. c, Exposure of a hydrophobic TiO$_2$-coated glass to water vapour. The formation of fog (small water droplets) blocked the view of the text on paper placed behind the glass. d, an antifogging surface produced by UV irradiation. The high hydrophilicity prevents the formation of water droplets, making the text clearly visible [204].

Another important application of TiO$_2$ is as the electrode of dye-sensitized solar cell (DSSC) [169, 205, 206]. DSSC is considered as a cost-effective alternative to silicon solar cells. Typically, mesoporous nanocrystalline TiO$_2$ is used in this application as the porous electrode to chemisorb dye molecules, and pores of the
film are filled with liquid electrolyte. Photo-excited dye molecules inject electrons into the TiO$_2$, and the injected electrons diffuse through the TiO$_2$ particle network to the collecting transparent conducting oxide (TCO) substrates. The redox species in the electrolyte transport holes from oxidized dye molecules to the counter electrode. The highest conversion efficiency of 11.1% for DSSC has been achieved by using TiO$_2$ as the electrode [207]. For the DSSC applications described above, the anatase phase TiO$_2$ is mainly used rather than rutile phase, as anatase phase has been generally recognized to have better photocatalytic ability and can give high quantum efficiency when used in DSSC devices [208].

7.1.2 Synthesis of TiO$_2$

In most applications of TiO$_2$ such as photocatalysis and DSSC, high surface area is needed for increasing the reaction area and thus the performance efficiency. The high surface area is achieved by using the material in the nanostructure form. Rutile phased TiO$_2$ nanowires can be synthesized by using vapour-liquid-solid (VLS) method, similar to the way described in Chapter 2 for ZnO nanostructure synthesis, but the process usually has to be carried out at a temperature above 1000$^\circ$C.

TiO$_2$ nanotubes can be produced by mainly three methods: chemical template synthesis, anodic oxidation of Ti foil and alkaline hydrothermal method. In chemical template synthesis, the TiO$_2$ nanotubes are prepared by sol-gel hydrolysis using solutions of Ti-containing compounds in the presence of templating agents, followed by polymerization of TiO$_2$ in the self-assembled template molecules or deposition of TiO$_2$ onto the surface of the template aggregates (usually porous alumina). The final step is the removal of templating agent and calcination of samples. The as-prepared nanotubes are amorphous, and after a calcination at 500$^\circ$C, it can transform to polycrystalline anatase. The disadvantage of this method is in most cases the
template material is sacrificial and needs to be destroyed after synthesis, thus increasing the cost of materials. This limits its applications in industry [209].

The anodic oxidation method was first reported to produce TiO₂ nanotubes in 2001 by Grimes and co-workers [210]. The self-organized TiO₂ nanotube arrays were formed by direct anodization of Ti in a H₂O-HF electrolyte. The as-prepared TiO₂ nanotubes were amorphous and, after calcination at 500°C, the crystal structure was reported to be a mixture of anatase and rutile [210]. Compared to the previous method, TiO₂ nanotubes produced by anodization have been effectively immobilized on Ti surface, and thus would be easier to use in the typical TiO₂ applications. However, the length of the nanotubes produce by this method was limited to be less than 2.4 μm, and may not be suitable for the DSSC application, which requires TiO₂ layer of more than 20 μm.

In the alkaline hydrothermal method, amorphous TiO₂ is treated with a concentrated solution of NaOH in a polytetrafluoroethylene-lined batch reactor at elevated temperature, followed by washing with water and HCl. Anatase, rutile, brookite and amorphous form of TiO₂ in polycrystalline can all be produced by this method [211]. The main disadvantage of this method is hazardous chemicals (NaOH, HCl) are used, which will cause additional environmental issues if being industrialized.

The most commonly used method to produce the TiO₂ porous layer for DSSC application is the so-called doctor-blade technique. Typically 0.02 to 0.07 g of polyethylene glycol (PEG) is added as a binder to 1 mL of the concentrated colloidal TiO₂ solution (11.wt.%) to increase the porosity. The colloidal TiO₂ solution is usually prepared by commercial TiO₂ powder, such as P25, ground with water, particle stabiliser such as acetyacetone, and non-ionic surfactant such as Triton X.
The colloidal TiO\textsubscript{2} solution is spread on a TCO substrate and then sintered at 450\textdegree C for 30min in air. The resulting TiO\textsubscript{2} film is transparent [212].

7.1.3 Comparison with ZnO

By examining research reports on TiO\textsubscript{2}, it can be found that most TiO\textsubscript{2} applications are related to its wide energy band gap, which can also be found from ZnO. Therefore, ZnO should be promising in similar applications as well. Moreover, ZnO has the advantages of easy formation of various nanostructures and high electron mobility compared to TiO\textsubscript{2}, which may make ZnO a better candidate in the DSSC applications. In fact, studies of ZnO in the same fields as TiO\textsubscript{2}, such as photocatalysis and DSSC, have already been carried out [213-215].

However, there are some advantages of TiO\textsubscript{2} that can not be found in ZnO, such as the excellent chemical stability [15] and high micro roughness [133], which are also important for delivering high performance in the applications mentioned above. Therefore, combining the advantages of TiO\textsubscript{2} and ZnO may be able to further increase the working efficiency of current TiO\textsubscript{2} based products, and synthesis ZnO/TiO\textsubscript{2} composite structures should be the way to achieve this.

Porous film is the most used structural form of TiO\textsubscript{2} in DSSC. ZnO itself can be used to form TCO substrate. If ZnO porous film can replace the TiO\textsubscript{2} layer in DSSC, due to the homogeneous junction, the electron diffusion from the porous electrode to the TCO should be enhanced. In photocatalytic applications, supported porous film has the advantages of reusability and reduction in the secondary contamination over nanopowders, and provides a large surface area at the same time. This is why synthesis of ZnO porous film and ZnO/TiO\textsubscript{2} porous film by wet oxidation is studied in this chapter.
7.1.4 Production of ZnO Porous Film

A number of the methods introduced in Chapter 2 can be used to produce ZnO porous film, but most of the produced films should be rather described as nanoparticle network or nanowire arrays. The practical ways to produce ZnO porous film for photocatalytic applications are sol-gel methods [216], doctor blade methods [215] and electro-chemical deposition (ECD) [140].

![Figure 7-2. Scanning electron microscopy (SEM) images of ZnO porous films produced by a) sol-gel method [216], b) doctor-blade method [215], c) electrochemical deposition with SDS added as surfactant [217], and d) electrochemical deposition with EDTA added as shape-control reagent [218].](image)

ZnO porous films have been produced by sol-gel method by using PEG as an organic template, Zn(CH₃COO)₂•2H₂O as a precursor, ethanol as the solvent and NH(C₂H₂OH)₂ as the chelating agent. Dip-coating method was used to coat sol on
the glass substrate with a drawing rate of 6 cm/min. After each dipping, the coated film was dried at 100°C in air for 10 min. The dipping processes were repeated 6 times, and then the films were calcined in air up to 500°C for 1 hr. It was found that the organic template PEG has the major impact on the formation of porous film. It was reported that 0.7 g PEG in 50 ml solvent favoured porous ZnO thin film formation [216]. The resulting ZnO porous film is shown in Figure 7-2a.

The doctor-blade technique is similar to the one introduced for TiO2 preparation. As Lu et al [215] reported, a mixture of HCl solution (2 ml, 0.1 M), dry ethanol (6 ml), acetylacetone (0.5 ml) and ZnO nanoparticles (1.0 g) were put into a PTFE container and then dispersed through a ball-milling process. The resulting pastes were dropped onto the substrate, and annealed at a temperature around 400°C for 1 hr to form the porous film. Figure 7-2b shows the resulting film.

ZnO crystalline film can be easily formed by ECD without any subsequent heat treatment. Porous film can be produced by using surfactant or shape-control reagent [218]. Sodium laurylsulfate (SDS) is normally used for ZnO porous film, which can self-assemble into aggregate to act as template at the solid-liquid interface of the substrate and catalyze the growth of ZnO [217].

Ethylene diaminetetraacetic acid [EDTA, (CH2N)2(CH2-COOH)4] was studied as a shape-control reagent. It works in the way that EDTA chelates strongly with Zn2+, and dramatically decreases the concentration of free Zn2+ in the solution. Thus, the electro-reduction of Zn2+ is relatively slow, and the newly deposited Zn has enough time to react with H2O or the carboxyl in EDTA before the aggregation of the later-deposited Zn. The formed nanoporous structures can be explained as the result of H2 bubbles functioning as a dynamic template during metal deposition. Figures 7-2c & 2d are the SEM images of the ZnO porous film formed by ECD by adding surfactant and shape-control reagent.
Although, electrochemical deposition is a low temperature and cost-efficient method for the ZnO porous film, it brings impurities into the ZnO film, and some of the impurities can prohibit the further application of films. For example, eosin Y bound to a ZnO film surface can make the absorption of dyes difficult for DSSC applications [217]. Moreover, the various chemical reagents may cause some possible environmental contaminations. Furthermore, the thickness of the electrochemical produced ZnO nanostructured films usually can only reach several microns, which is not thick enough for applications such as DSSC. Accordingly, an easy and efficient approach is desirable for thick ZnO porous film preparation, which is suitable for real applications.

This chapter demonstrates that wet oxidation is an alternative method to produce ZnO porous film, as well as ZnO/TiO₂ hybrid porous film, with a high thickness and uniformly distributed porosity.

7.2 ZnO & ZnO/TiO₂ Porous Film Preparation

7.2.1 Precursor Film Preparation

Reactive direct current (DC) magnetron sputtering (MS) was used to prepare the partial oxidized Zn precursor film. All the experimental parameters were the same as those in the previous chapter, except that O₂ was introduced into the chamber with Ar to conduct reactive sputtering. For preparation of ZnO/TiO₂ porous film, the due targets system described in Chapter 3 was adopted to mix Ti or TiO₂ into the precursor films. The Zn target was installed at the position labelled as Target 1 in Figure 3-2. Two types of targets were used at the position of Target 2: metallic Ti (99.99%) and TiO₂ (99.99%), DC power was forwarded to both targets at the same time.
The applied DC current was varied independently for each target in order to control the deposition rate of each material. The deposition time varied from 10 min to 30 min, and the O\textsubscript{2} concentration varied from 5% to 30%. The surface and cross-section morphologies of precursor films were examined with scanning electron microscopy (SEM). The phase analysis was conducted by using X-ray diffractometer (XRD).

### 7.2.1.1 Zn-ZnO Composite Precursor Film

![SEM images of Zn-ZnO composite precursor film MS deposited with various O\textsubscript{2}%.](image)

Figure 7-3. SEM images of Zn-ZnO composite precursor film MS deposited with a) 5\%O\textsubscript{2}, b) 15\%O\textsubscript{2}, c) 25\%O\textsubscript{2}, and d) 30\%O\textsubscript{2}.

Figure 7-3 shows the surface morphologies of the precursor films deposited with various O\textsubscript{2}%. With 5\% O\textsubscript{2}, the film was made of small particles with the individual hexagonal-shapes, and spaces can be seen between the particles. When O\textsubscript{2}% increased to 15\%, distinct particles can still be observed, but many of them are connected to form a network with significantly increased pore size. When O\textsubscript{2}%
increased to 25%, the particle size reduced, as well as the pore size, but they appear more uniformly distributed across the surface. Increasing O₂% to 30%, the resulting film became very smooth and consist of small particles.

Figure 7-4. XRD patterns of Zn-ZnO composite films prepared by various O₂%.

![XRD patterns of Zn-ZnO composite films prepared by various O₂%](image)
Figure 7-4 shows the XRD patterns of the precursor films prepared with O₂% from 5% to 30%. It can be noted that the films shown in Figures 7-3a, 3b & 3c, with porous structures, all gave dominant Zn peaks in XRD patterns. When increasing O₂%, from 5% to 25%, the intensities of Zn peaks decreased, indicating the quantity of Zn in the films was reduced. Meanwhile, the full width at half maximum (FWHM) became larger, suggesting that the Zn grain size has decreased, which is consistent with the observation from SEM images. As the Zn peaks weakened by increasing O₂%, the peaks related to ZnO became much clearer to see, especially at 25% O₂. This means that the percentage of ZnO in the precursor films rose with O₂%. The XRD patterns of precursor film prepared by 5%, 15% and 25% O₂ prove that the precursor films with porous feature have a Zn-ZnO composite structure.

When further increasing O₂% by only 1% to 26%, the Zn peak totally disappeared, leaving only the ZnO (002) peak detected. The film deposited with 30% O₂ also gives a similar XRD pattern, and thus the dense film shown in Figure 7-3 should be a complete ZnO film. The fact that only ZnO (002) peak was detected, indicates that the ZnO film growth has a preferential direction, which can also be found from the ZnO film deposited by MS with a ZnO target. This infers that with 26% or more O₂ introduced to the sputtering process, all the Zn atoms leaving the Zn target have been oxidized to form ZnO molecules before reaching the substrate so that the preferential grown dense ZnO film has formed. Therefore, to get porous films, it is important have partially oxidised Zn film by controlling the O₂% in the working atmosphere.

### 7.2.1.2 Partially Oxidized Zn-Ti Precursor Films with Zn/Ti Dual Targets

The previous section shows that Zn-ZnO composite porous precursor films can be produced. In this section, the process is further developed to produce ZnO/TiO₂
composite precursor films. Table 7-1 give a list of the experiment parameters combination used for preparation.

<table>
<thead>
<tr>
<th>sample#</th>
<th>DC Current</th>
<th>O2%</th>
<th>Deposition Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T1 (Zn)</td>
<td>T2 (Ti)</td>
<td>(min)</td>
</tr>
<tr>
<td>1-1</td>
<td>0.5</td>
<td>0.5</td>
<td>20%</td>
</tr>
<tr>
<td>1-2</td>
<td>0.5</td>
<td>0.5</td>
<td>20%</td>
</tr>
<tr>
<td>1-3</td>
<td>0.5</td>
<td>0.5</td>
<td>10%</td>
</tr>
<tr>
<td>1-4</td>
<td>0.4</td>
<td>0.75</td>
<td>10%</td>
</tr>
<tr>
<td>Set1</td>
<td>1-5</td>
<td>0.4</td>
<td>1.0</td>
</tr>
</tbody>
</table>

DC current of 0.5 A and 20% O2 was used first, as shown in the last section that the reactive sputtering Zn target with the current of 0.5 A and O2% less than 25% would give porous ZnO film. With 5 min deposition time, the film has a black glassy appearance, which was usually due to the film (film 1-1) being very thin.

Figure 7-5a shows the surface morphology of this film. It appears that the film consists of very small and irregularly shaped grains and many elongated particles. The plot in Figure 7-5a is the energy-dispersive X-ray spectroscopy (EDX) spectrum of film 1-1. The Ti peak is very weak in this spectrum, indicating that the deposition rate of Ti was much slower than that of Zn at the same DC current. Peaks for Si and Ca can be detected and they should be from the glass substrate, inferring that the film was so thin that the electron beam could penetrate to the substrate.

Extending the deposition time to 10 min produced film 1-2. The film has a black and rough appearance, closer to that of the Zn-ZnO composite precursor for porous film. Its EDX spectrum (Figure 7-5b) shows the Si and Ca peaks have almost disappeared due to the increasing film thickness. The Ti peak seems even weaker than Film 1-1, almost falls into the background, suggesting that the increasing deposition time does not increase the relative concentration of Ti compared to Zn.
The SEM image in Figure 7-5b shows film 1-2 is covered by larger clusters with irregular shapes, and the elongated small particles still exist. The film looks not as porous as the Zn-ZnO composite film prepared under the same conditions. This means that either the O₂ concentration was not high enough, and little ZnO was formed to induce the porosity, same scenario as the Zn-ZnO composite film prepared with 5% O₂, or the O₂ concentration was too high and most of the Zn had been oxidized to compact ZnO clusters, which happened to the Zn-ZnO composite film prepared with 26% O₂ or higher O₂ concentration.

The latter scenario is more likely to occur, and thus film1-3 was prepared by decreasing the O₂% to 10%. Figure 7-5c shows that the surface morphology of film1-3 changed dramatically. The wire-shaped network structure formed to create high porosity, similar to the Zn-ZnO composite porous film, which means 10% O₂ is more favoured for the porous structures formation. However, this porous structure contains larger clusters when compared with the Zn-ZnO composite porous films, indicating the particle agglomerate under these deposition conditions.

The EDX spectrum demonstrates that the O peak is weaker than that of film 1-2, corresponding to the lower O₂% introduced during the deposition. The Ti peak is more obvious in the EDX curve, despite the deposition current remaining unchanged. This could be due to the metallic film deposition rate (Zn or Ti) being much higher than the related metallic oxide film deposition rate by reactive sputtering with O₂ working gas. The critical O₂% for Ti being completely oxidized to TiO₂ could be between 10% and 20%, which is lower than that of Zn (25-26% discussed in Section 7.2.1.1). Thus when the O₂% decreased to 10%, the Ti deposition rate increased even though the current was the same, resulting in the stronger Ti peak signal in the related EDX spectra.
Chapter 7. ZnO and ZnO/TiO$_2$ Porous Films

Figure 7-5. The EDX spectra and SEM images of the partially oxidized Zn-Ti precursor films: a) film 1-1, b) film1-2, c) film 1-3, d) film 1-4, and e) film 1-5. Their deposition conditions are summarized in Table 7-1.

It has been demonstrated that the Ti deposition rate is much slower than that of Zn. Thus, in order to increase the Ti composition in the film, the deposition current
of Zn was reduced to 0.4 A, and the current of Ti raised respectively to 0.75 A and 1.0 A to produce film 1-4 and film 1-5.

The surface morphology of film 1-4 shows very uneven features (Figure 7-5d). Small grains, large round clusters, and elongated grains can all be seen on the surface. This could be due to the Zn and Ti forming separate phases during the deposition. The EDX spectrum of films 1-4 and 1-5 show that the Ti peaks became much stronger (Figure 7-5d), confirming that Ti composition increased. However, the Si and Ca peaks appear again in the spectrum, indicating that the film became thinner. Thus, the increase in Ti deposition rate could not compensate for the reduced amount of Zn deposition.

Increasing the current to Ti target further to 1.0 A caused the film surface to be covered by large clusters (Figure 7-5e). The EDX spectrum shows the Si & Ca peaks became very weak, an indicator that the film thickness has increased, which should be mainly due to the increase in the Ti deposition rate. It can be seen that the addition of Ti prevented the formation of the porous structure obtained when only a Zn target was used. Only film 1-3 shows a relatively high porous structure.

### 7.2.1.3 ZnO-TiO2 Composite Precursor Films with Zn/TiO2 Dual Targets

#### Table 7-2. The experimental conditions for Set-2 samples.

<table>
<thead>
<tr>
<th>sample#</th>
<th>DC Current</th>
<th>O2%</th>
<th>Deposition Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1 (Zn)</td>
<td>T2 (TiO2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-1</td>
<td>0.3</td>
<td>0.25</td>
<td>20%</td>
</tr>
<tr>
<td>2-2</td>
<td>0.5</td>
<td>0.25</td>
<td>20%</td>
</tr>
<tr>
<td>2-3</td>
<td>0.5</td>
<td>0.25</td>
<td>20%</td>
</tr>
<tr>
<td>2-4</td>
<td>0.5</td>
<td>0.25</td>
<td>0%</td>
</tr>
<tr>
<td>2-5</td>
<td>0.5</td>
<td>0.25</td>
<td>10%</td>
</tr>
</tbody>
</table>

The previous section demonstrates that reactive sputtering Zn and Ti targets could not produce highly good porous precursor films. Thus the Set 2 films were prepared by
replacing the Ti target with a TiO$_2$ target. The TiO$_2$ would not react with O$_2$ during the sputtering deposition, and thus should have less effect on the formation of the Zn-ZnO composite porous structures. The experimental conditions have been summarized in Table 7-2.

**Figure 7-6. The SEM images showing the surface morphologies of: a) film 2-1, b) film 2-2, c) film 2-3, d) film 2-4, and e) film 2-5. The deposition conditions are summarized in Table 7-2.**

DC current of 0.25 A was used on the TiO$_2$ target for the preparation of all Set 2 films, and 0.3 A was forwarded to the Zn target for film 2-1 deposition with a deposition time of 10 min. Figure 7-6a shows that film 2-1 was formed with densely
packed small grains. Increasing the DC current forwarded to the Zn target to 0.5 A did not change the film structure significantly with the same deposition time, as shown in Figure 7-6c (film 2-3).

However, the porous structure formed after extending the deposition time to 30 min (film 2-2), as shown in Figure 7-6b. This could be because that at the beginning of the deposition, the O₂ concentration in the chamber was high enough to completely oxidize the Zn atoms came from the Zn target, but as the deposition progressed, the O₂ supplying rate is lower than the consumption rate. Hence, the O₂% would decrease over time, so that the Zn atoms could not be completely oxidized to form the porous structure.

The XRD spectrum of film 2-2 shows both Zn and ZnO peaks, with no preferential orientation, indicating that the reactive sputtering deposition yields partially oxidized Zn film (the XRD patterns is shown in Figure 7-11, together with its XRD patterns after wet oxidation). Decreasing the introduced O₂ percentage to 10%, can lead to the formation of a porous structure within 10 min deposition time (film 2-5 shown in Figure 7-6e). This confirms the mechanism described above: as the O₂ supply is reduced, it takes less time to start forming porous structures. Thus, even with 10 min deposition time, porous film can still be formed. However, if no O₂ was introduced, the deposited film would not be porous (film 2-4), as shown in Figure 7-6d. This infers that only co-sputtering TiO₂ would not induce the porous structure.

7.2.2 After Oxidation

7.2.2.1 Zn-ZnO Composite Precursor Films after Oxidation

The Zn-ZnO composite precursor films prepared in Section 7.2.1.1 were wet-oxidized at 450°C for 1 hr to produce ZnO porous films.
Figure 7-7. The surface morphologies of Zn-ZnO composite film MS deposited with a) 5% O₂, b) 15% O₂, and c) 25% O₂, after wet oxidation at 420°C for 1 hr.

The precursor films shown in Figure 7-3a, b and c were converted to ZnO films after wet oxidation. Figure 7-7 shows the surface morphologies of the resulting films. The Zn-ZnO composite film deposited with 5% O₂ (Figure 7-3a) was oxidized to a
relatively dense film (Figure 7-7a). The Zn particles seem to have expanded during the oxidation to close the gaps between them.

For the film deposited with 15% O\textsubscript{2} (Figure 7-3b), the porosity remained at a similar level after wet oxidation (Figure 7-7b). The particle size was reduced after the oxidation. But it seems that during the oxidation the ZnO crystal grew out of the original Zn particles to form short wires connected to each other to form a network.

The surface morphology of the precursor film deposited with 25% O\textsubscript{2} did not change greatly after wet oxidation, nor did the porosity (Figure 7-7c). Generally, the porosity of the Zn-ZnO composite precursor film remains at a similar level after the wet oxidation. Therefore, the porosity of the ZnO film can be tuned by controlling the O\textsubscript{2}% during the reactive sputtering process for precursor preparation.

Figure 7-8. The surface morphologies of Zn-ZnO films prepared with 15% O\textsubscript{2} after oxidation in dry oxygen at 450\textdegree C for 1 hr. a) high magnification, b) low magnification.

The Zn-ZnO precursor film prepared with 15% O\textsubscript{2} was also oxidized in dry O\textsubscript{2} for the same duration and temperature as the wet oxidation. However, the porosity was not preserved after the dry oxidation. Figure 7-8 shows the surface morphology of the film after dry oxidation. It can be seen that many of the precursor particles aggregated together to form large clusters. Some gaps still existed between the clusters, but overall the film appears much denser than those from wet oxidation,
implying that water vapour is essential for maintaining the porosity of the films during the oxidation process.

7.2.2.2 Oxidation of Zn-Ti Precursor Films by Zn/Ti Dual Targets

As demonstrated in the previous section, the porosity of the oxide film is mainly determined by the microstructure of its precursor. Therefore, it can be predicted that,
even after oxidation, porous film would not be formed easily from Set-1 precursor films, as only film 1-3 had certain level of porosity.

Figure 7-9 shows the morphologies of films 1-1 to 1-5 after wet oxidation. Figures 7-9a & 9b are the images for film 1-1 after wet oxidation for 1 and 2 hr, respectively. It can be seen that the increase in oxidation time did not change the morphology greatly.

![Figure 7-10. The cross section view of the films: a) 1-1, b) 1-2, c) 1-3 and d) 1-4, all after 1 hr wet oxidation.](image)

The SEM images show that after wet oxidation, none of the precursor films gave a good porous structure. Even for film 1-3, the porosity is not very high a the wired network expanded after oxidation and blocked most of the space (Figure 7-9d). The films converted from films 1-4 and 1-5 gave similar morphologies as shown in Figure 7-9e & 9f. Figure 7-10 shows the cross section view of films 1-1, 1-2, 1-3 and 1-4 after 1 hr oxidation, showing few pores were formed by the oxidation.
7.2.2.3 Oxidation of Zn-TiO₂ Precursor Films by Zn/TiO₂ Dual Targets

As demonstrated in Section 7.2.2.1, only precursor films with a porous structure would form porous film after the wet oxidation. Therefore, film 2-2 and film 2-5 were investigated further with wet oxidation.

![Figure 7-11. XRD patterns of: a) film 2-2, and b) film 2-2, all after wet oxidation.](image)

The XRD patterns in Figure 7-11 shows both Zn and ZnO peaks, with no preferential orientation for film 2-2. After 1 hr wet oxidation, all Zn peaks vanished, indicating that residual Zn had been transformed to ZnO. No obvious TiO₂ related XRD peak was detected for the as-deposited Zn-TiO₂ film. This is probably due to TiO₂ not being crystallized in the as-deposited Zn-TiO₂ film. However, even after exposure at 450°C for 1 hr, there was still no TiO₂ detected. This suggests that the
TiO$_2$ concentration may have been too low to be detected by XRD. The XRD patterns of film 2-5 shows similar features.

Figure 7-12. a) The cross section and b) surface morphology of film 2-2 after wet oxidation.
Figure 7-12 shows the cross section and top surface morphology of film 2-2 after wet oxidation. The cross section view shows the thickness of the film is about 50 µm, and the porosity is uniformly distributed throughout the thickness. There is a dense layer of oxide at the bottom, which should have formed when the O₂ concentration was high enough to completely oxidize the Zn atoms at the beginning of sputtering deposition. The pore size is about 100 nm. The surface of the film was covered by short rods with nano-sized cluster on their tips, which was not observed before the oxidation.

Figure 7-13 displays the cross section and surface morphologies of film 2-4 after wet oxidation. The porous structure is finer than film 2-2, but the thickness is much smaller than film 2-2, only about 2 µm. The nano-cluster structures formed on film 2-2 could not be observed on film 2-4.

![Figure 7-13. a) Cross section and b) surface morphologies of film 2-4 after wet oxidation.](image)

The crystal structure of the nano-clusters formed on the surface of film 2-2 after wet oxidation was studied with a high resolution transmission electron microscope (HRTEM). The TEM image (Figure 7-14a) shows that the cluster on the tip is polycrystalline. Another HRTEM photo (Figure 7-14b) was taken on the grain boundary area. The lattice spacing for the two adjacent grains are 0.2377 nm (upper-
left) and 0.2430 nm (bottom-right), corresponding to the [004] and [103] planes of TiO$_2$ anatase phase crystal, respectively. Therefore, the TEM result proves that the small cluster on the tip of the nanorod is TiO$_2$ in anatase phase.

Figure 7-14. a) TEM image of a cluster structure on the film surface, and b) the HRTEM image taken at the boxed area of a).
These TiO\(_2\) nano-clusters can be formed by agglomeration of the amorphous TiO\(_2\) particles that had been dispersed into the ZnO matrix at the sputtering stage through a thermal diffusion process during the wet oxidation. The wet oxidation temperature is 420\(^\circ\)C. It has been reported that most amorphous TiO\(_2\) can transform to anatase at above 350\(^\circ\)C after 1 hr annealing [82], and the anatase-rutile transformation temperature is around 600\(^\circ\)C [199]. Therefore, the TiO\(_2\) crystal was formed in anatase phase but not rutile.

Although the SEM can only observe anatase nano-clusters on the surface, TiO\(_2\) nanoparticles should also exist in the porous film. The reason that the XRD result did not show any TiO\(_2\) anatase peak could be due to the quantity and the size of the TiO\(_2\) being too low and small to be detected. However, XPS analysis detected a very week Ti 2p peak, and the Ti atomic concentration was calculated to be 0.37\% using XPS spectra.

7.2.3 Discussions

7.2.3.1 Formation of Porous Structure during Magnetron Deposition

It has been demonstrated that without introduction of O\(_2\), metallic Zn film would form and, with excess O\(_2\), close packed ZnO film would form. The porous precursor films can only be obtained when only partial Zn was oxidized during the sputtering deposition.

For normal sputtering deposition of ZnO, the initial ZnO particles that reached the substrate would form the initial nucleation sites, and the later coming ZnO species would rest on those nucleation sites in the orientation to match the crystal lattice of the nucleation sites that follow the minimum energy principle. Finally, the close packed and dense films were deposited. However, when a portion of Zn atoms
were oxidized, the resulting ZnO molecules would deposit on the substrate together with the un-oxidized Zn, forming Zn or ZnO crystal grains respectively as the initial nucleation sites.

As these two types of materials were deposited at the same time, their crystal grains would mix together. Therefore, the crystal lattice of either Zn or ZnO would discontinue over a short period, and the later deposited species (Zn or ZnO), would not always rest on the lattice-matched and energy-favoured sites (e.g. ZnO species deposited on Zn crystals and vice versa). Thus, the continued deposition would be random without preferential orientation, resulting in the final porous structure. If the percentage of either Zn or ZnO is too high, the structure tends to be more ordered, so there is an optimum oxygen concentration of around 15% O$_2$ that can produce the maximum porosity than any other O$_2$% used.

With the Zn/Ti dual targets setup, it was difficult to produce porous precursor film. With reactive sputtering Zn and Ti at the same time, Ti is more reactive with O$_2$ than Zn, as Ti has a more negative $\Delta G^0$ value than Zn, shown on the Ellingham diagram, as well as more negative redox potential. Hence, the majority of the O$_2$ introduced into the chamber reacted with Ti, and less Zn was oxidized during the deposition. In this case, continuous Zn crystal phase were likely to form, and resulting in less porosity in the film. The evidence can be found from the fact that increasing the Ti deposited rate compared to Zn (e.g. film 1-3 to 1-5) led to denser films.

With the Zn/TiO$_2$ dual targets setup, the deposition of TiO$_2$ would not compete with Zn for reacting with O$_2$. Therefore, the same oxidation process of Zn as happened when using a single Zn target would not be interrupted and thus would form a similar porous structure. For this situation, the TiO$_2$ particles were mixed to the ZnO-Zn composite matrix.
7.2.3.2 Microstructures after Oxidation

It has been demonstrated that wet oxidation is better than dry oxidation for preserving and enhancing the porous structures. The presence of water vapour promoted the outward transportation of Zn-containing components [180]. This allowed Zn to diffuse out of the precursor particles and form the wired network structures shown in Figure 7-5b. The mechanism is similar to the water assisted surface diffusion discussed in Chapter 4 by Figure 4-11 to 4-14. For dry oxidation, fast diffusion was not observed, so the precursor particles were mostly oxidized at their original states, and aggregated together with reduced pore size and porosity.

The precursor films prepared by Zn and Ti target could not form porous films after wet oxidation, mainly because the precursor films were not porous. Furthermore, no other nanostructures, such as nanowires/nanobelts, formed after the wet oxidation, which should be caused by the mixing of Ti species to the Zn films. This is because that the mixed Ti could depress or even inhibit the Zn atoms’ diffusion, which is essential for the initial growth stage of nanowires/belts in the wet oxidation process, as discussed in Chapter 4.

For the precursor films prepared by Zn/TiO₂ dual targets system, the formation of a porous structure was not affected by the TiO₂ mixing. Thus after wet oxidation the ZnO/TiO₂ film still remained porous. For this situation, the TiO₂ nano-clusters with anatase phase were formed after the wet oxidation process (film 2-2). They could have originated with the diffusion of the TiO₂ particles that were mixed into the ZnO matrix during sputtering, and agglomerated together during the oxidation. However, the same structure could not be found in film 2-4 after oxidation, suggesting that the formation mechanism of the TiO₂ nano-clusters was complicated, and requires more investigation.
7.3 Optical Properties

7.3.1 UV-VIS Absorption Test

The diffuse reflectance test (Shimadzu 2100 UV/vis) was adopted to obtain the absorption spectra of the porous films. BaSO$_4$ was used as a reference for all test samples. Figure 7-15 illustrates the plots of the absorption curves of ZnO porous films (15% O$_2$) produced from dry oxidation, wet oxidation, and ZnO-TiO$_2$ porous film by wet oxidation (film 2-2). The absorption edges of these three films are located between 370 nm to 390 nm.

![Figure 7-15. The UV-VIS absorbance spectra of dense ZnO film, porous ZnO film, and porous ZnO/TiO$_2$ film.](image)

However, the inserted plot shows that the optical gap of wet oxidation produced ZnO porous films red-shifted from the one produced by dry oxidation. In fact, ZnO produced from wet oxidation has higher porosity, and hence has a larger surface area,
which could be the reason of the red shift, since it is understood that the band gap energy ($E_g$) of semiconductors is also affected by the surface condition of the material. The $E_g$ of ZnO-TiO$_2$ porous film is further red shifted from the wet oxidation-produced ZnO porous film, which should mainly come from the mixing of TiO$_2$ compound since TiO$_2$ has a smaller band gap than ZnO crystals.

### 7.3.2 PL Properties

The room temperature photoluminescence (PL) test was carried out on the ZnO and ZnO-TiO$_2$ porous film with a $\lambda = 325$ nm laser source. Figure 7-16 displays the room temperature PL spectra of a porous ZnO film produced by wet oxidation, as well as a dense ZnO film by MS. It is clear to see that the peak position of the porous ZnO PL spectrum is red shifted compared to the dense ZnO film (380 nm vs. 377 nm), which is mainly caused by the large surface area (as mentioned in the previous section). The PL peak of the porous ZnO is also broader than the dense film, resulting from the crystal quality and surface effect. The peak 388 nm on the porous ZnO PL spectrum comes from the system noise.
Figure 7-16. The room temperature PL spectra of porous and dense ZnO films at the UV region.
Chapter 7. ZnO and ZnO/TiO₂ Porous Films

PL measurement shows that the ZnO-TiO₂ porous film has major light emission at 380–450 nm (Figure 7-17). The inset graph shows that the curve can be deconvoluted into several peaks; they are at 383, 393, 404, 412, 424, 434 and 450 nm. The peak at 383 nm is from ZnO [70], and the peak at 393 nm coincides with the E₉ of anatase phase TiO₂ crystals (3.18 eV/390 nm [219], and 3.20 eV/387 nm [200]). For the three peaks located at 404, 412 and 424 nm, there is no clear explanation for their origin, as in different literatures each of these three peaks has been explained by using the same origin: self-trapped excitons localized at TiO₆ octahedral sites (404 nm [70], 412 nm [220], 424 nm [221]). However, these three peaks appear together from this ZnO/TiO₂ sample, probably indicating the enhanced self-trapped excitons induced by the combination of ZnO. The other peaks with longer wavelength could be attributed to the oxygen vacancies and the surface states [14, 221].

![Figure 7-17. Room temperature PL spectrum of the ZnO/TiO₂ porous film and the insert plot shows the fitted curves.](image_url)
It is interesting to note that the light emission from ZnO is weaker compared to that from TiO₂, despite the ZnO quantity being much greater than TiO₂. This phenomenon can be well explained by the recently reported coupling mechanism [14]. According to Zou’s explanation, the TiO₂ nano-clusters on the film surface may have absorbed some photons emitted from ZnO, and the TiO₂ nano-clusters were thus excited by both the laser photons and UV emission from the ZnO. This so-called resonant effect for the PL process may be the reason that the TiO₂ related peaks are more intensive than ZnO. The enhanced PL property suggests that this ZnO/TiO₂ may have good performance in the photocatalytic applications such as DSSC and decomposition of organic compounds, or water splitting for hydrogen productions.

7.4 Applications

The large surface area, broad light absorption range in UV and visible light (VIS) make the porous ZnO/TiO₂ an ideal material for photocatalytic applications. Some prototype application tests were carried out.

7.4.1 Photo Degradation

The basic photophysical and photochemical principles underlying photocatalysis are well established and have been reported in many literatures [203, 208, 211, 222-224]. Figure 7-15 illustrates the photophysical and photochemical process over photon activated semiconductor photocatalyst.

Photocatalytic reaction is initiated when an electron in the valence band of the semiconductor photocatalyst is excited to the conduction band by absorbing photo energy. The exciting photo energy, \( hν \), has to equal or exceed the band gap of the semiconductor photocatalyst (SC). The excitation leaves a hole in the valence band (photoholes), and thus the electron and hole pair (\( e^- \cdot h^+ \)) is generated. The electrons
in the conduction band and the holes in the valence band can be surface tripped, and
reacts with the species adsorbed to the SC surface. It has been reported that these
reactions can successfully compete with the picosecond electron-hole recombination
process [225]. Photoholes have great potential to oxidize organic species directly or
indirectly via the combination with OH• predominant in aqueous solution. The
following chain reactions describe the degradation process [171]:

\[
\begin{align*}
\text{TiO}_2 + \text{hv} & \rightarrow 2e^- + 2h^+ \quad (7-1) \\
h^+ + \text{H}_2\text{O} & \rightarrow \text{OH}\cdot + 2\text{H}^+ \quad (7-2) \\
\text{R-H} + \text{OH}\cdot & \rightarrow \text{R}^\cdot + \text{H}_2\text{O} \quad (7-3) \\
\text{R} + h^+ & \rightarrow \text{R}^+ \rightarrow \text{Degradation products} \quad (7-4)
\end{align*}
\]

Figure 7-18 Schematic photophysical and photochemical processes over photon
activated semiconductor cluster: (p) photo-generation of electron/hole pair, (q)
surface recombination, (r) recombination in the bulk, (s) diffusion of acceptor and
reduction on the surface of SC, and (t) oxidation of donor on the surface of SC
particle [171].
An important parameter influencing the performance of photocatalyst is the surface morphology of SC. Vinodgopal and Kamat reported the dependence of the photo-degradation rate on the surface coverage. In other words, only the molecules that are in direct contact with the catalyst surface undergo photocatalytic degradation [226]. Therefore, achieving a high surface area is essential for enhancing the photocatalytic performance of the photocatalyst.

7.4.1.1 Estrone

Estrone was chosen as the candidate for photo-degradation test. Although the test of photo degradation on estrone is not as easy to conduct as those tests on dye chemicals such as Bromo-Pyrogallol Red (Br-PGR), it has more practical significance for this study.

Estrone with a chemical formula of $C_{18}H_{22}O_2$ is one of the natural estrogens, and is one of the endocrine disrupting chemicals (EDC) or endocrine disruptors (EDs). It has the potential to interfere with the endocrine activity of the natural hormones both in animals and in humans. EDCs have been detected in wastewater treatment plant effluent [227] and reported to affect environments biologically at very low concentration [228]. Therefore, study on the degradation treatment for EDCs is focused on the minimizing its negative effects and it is particularly relevant to New Zealand and Australia. The highly developed dairy industry in New Zealand means large number of dairy farms, which have become a major waste source. It has been reported that the New Zealand livestock population excretes about 40 times more waste than the human population, and the animal effluent contains a high concentration of natural EDCs including estrone. There is no treatment to remove EDCs from the waste water currently, and minimizing the negative effects of EDCs
mainly relies on the dilution, sorption, and degradations that occur naturally within the ecosystem [229].

7.4.1.2 Degradation under UV Irradiation

The performance of ZnO and ZnO/TiO$_2$ porous films as photocatalysts was firstly tested by degrading estrone under 365nm wavelength UV light source. The Zn-ZnO composite films deposited with 20% O$_2$ for 30 min were used as the precursor for wet oxidation to prepare the ZnO porous films. The thickness is about 50 µm, similar to film 2-2. ZnO/TiO$_2$ porous films have the same microstructure as film 2-2, as shown in Figure 7-12. The substrates of the films are glass with dimensions of 15 mm × 15 mm.

![Figure 7-19. Concentration profiles of estrone solution under UV irradiation without catalyst (black line), with ZnO porous film as catalyst (red line), and with porous film ZnO/TiO$_2$ as catalyst (green line).](image-url)

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At the beginning of the degradation test, the ZnO and ZnO-TiO$_2$ films were immersed in 10 ml estrone aqueous solution with concentration of 0.3 ppm. The estrone solutions with films were kept in the dark for 30 min before exposure to UV irradiation, giving time for the absorption of estrone to the films reaching equilibrium, so that the measured concentration change during UV irradiation would be solely caused by photo-degradation. An 18 W UV lamp ($\lambda = 365$ nm, Osram) was used as the light source. The exposure time under the light was 4 hr. The distance from the film to the solution surface was fixed in all experiments to maintain a consistent attenuation factor for the incident light. A blank experiment without photocatalyst in the solution was conducted as a reference. For each solution, 300 µL fluid was sampled at the time point of -30 min, 0 min, 30 min, 60 min, 120 min, 180 min, and 240 min, where 0 min is the starting point of UV irradiation. The estrone concentration was tested by High Performance Liquid Chromatography (HPLC, Agilent 1100 series).

Figure 7-19 displays the test results. The $C/C_0$ on the y-axis represents the ratio of the measurement of estrone concentration at each sampling time point to the original concentration. The estrone concentration of the blank solution without any catalyst increased over the time period. This could result from the evaporation of water in the solution, which decreased the total volume of the solution. Even though the absolute amount of estrone did not change, the appeared concentration was raised.

With ZnO or ZnO/TiO$_2$ porous film as photocatalysts, estrone concentration kept decreasing over the 4 hr period and more than 60% of estrone had been degraded at the end of UV irradiation time. The estrone degradation curve catalyzed by ZnO-TiO$_2$ porous film has the same trend to that with the ZnO catalyst, and the degradation curve is slightly lower than that of ZnO, indicating the ZnO-TiO$_2$ porous film has better photocatalytic performance. However, the difference between these
two curves (33% vs. 38% at 240 min) is not large enough to tell whether it is caused by the addition of TiO$_2$. It could be due to the amount of TiO$_2$ being too small, as XPS showed that the Ti atomic concentration is only 0.1%.

It should be noted that the wavelength of the UV light is 365 nm, so the photo energy is higher than the band gap of both ZnO and TiO$_2$. One of the possible advantages of the ZnO/TiO$_2$ porous film, however, is the absorption of visible light demonstrated by the UV-VIS and PL test, which cannot be shown using this UV light source. Therefore, this test can only demonstrate that the ZnO and ZnO-TiO$_2$ porous films have similar photocatalytic abilities under UV light.

7.4.1.3 Degradation under UV-VIS Irradiation

Figure 7-20. The incident light spectrum on the solution surface: curve (a) measured without a filter, and curve (b) measured with a UV filter.
The catalytic performance of ZnO and ZnO/TiO$_2$ porous films was then tested under UV-VIS light source. ZnO and ZnO/TiO$_2$ porous films have the same structures with those used in the UV degradation test described above. The experiment setup and test procedure are the same as the previous one, but the degradation time was changed to 3 hr, and the light source was changed to a 300 W UV-VIS lamp ($\lambda \geq 280$ nm, Osram ultra-vitalux). The incident light intensity on the solution surface was measured by a radiometer (IL1700, International Light, USA), and the curve (a) in Figure 7-20 with blue colour shows the measured light spectrum.

![Figure 7-20. Concentration profiles of estrone solution under UV-VIS light irradiation without catalyst (black line), with ZnO porous film as catalyst (red line), and with ZnO/TiO$_2$ porous film as catalyst (green line).](image)

Figure 7-21 illustrates the test results. Without the presence of the ZnO/TiO$_2$ porous film, the estrone concentration also went down in the 3 hr period. This is due to
the direct photolysis of estrone. Estrone was found to be photolytic under short wavelength UV light ($\lambda = 254$ nm) [230]. Although the spectrum of the incident light (curve (a) in Figure 7-20) does not shown any light intensity below 300 nm, this is because the measuring sensitivity of the radiometer is poor for light with wavelength below 300 nm.

However, with ZnO and ZnO/TiO$_2$ film as photocatalysts, estrone concentration decreased rapidly and more than 90% of the estrone had been degraded at the end of the 3 hr UV-VIS irradiation. This result shows that the ZnO/TiO$_2$ porous film has good photocatalytic behaviour in the UV-VIS light range. The test result still does not show a big difference in the catalytic ability between ZnO and ZnO/TiO$_2$. The incident light has a large composition of UV light, so the major degradation may be caused by UV light, and thus the effect of the visible light becomes small. The low concentration of TiO$_2$ can also be attributed to the cause.

### 7.4.1.4 ZnO/TiO$_2$ Porous Film by Sol-Gel Method

Two types of tests can be performed to clearly examine the effect of TiO$_2$ on the photocatalysis efficiency of the porous film. One is to conduct the degradation test under visible light, so that the effect of UV light can be eliminated. The other is to increase the TiO$_2$ composition in the porous film to see if the quantity of TiO$_2$ has a significant effect on the degradation reaction. As explained in Section 7.2, it is difficult to increase the concentration of TiO$_2$ while still maintaining a porous structure by the sputtering-wet oxidation method. Thus, the sol-gel method was used to add extra TiO$_2$ into the porous film.
ZnO porous film was immersed in the TiO$_2$ sol and placed under UV irradiation for 2 hr, so that the TiO$_2$ sol could thoroughly seep into the pores of the films. ZnO film can exhibit strong hydrophilic properties under UV irradiation, which is helpful for the TiO$_2$ absorption into the films. The film was then spun at 6000 rpm for 30 sec to remove the extra sol, and followed by annealing at 450°C for 1 hr to crystallize TiO$_2$. The SEM image in Figure 7-22 shows that the final porosity was retained after this treatment, although it had certainly decreased compared to the original ZnO porous film (Figure 7-7b). A stronger Ti peak was detected by the EDX, and the XPS shows the Ti concentration is 4.9%, much higher than that of ZnO/TiO$_2$ (film2-2). Therefore, this method is successful for increasing the TiO$_2$ composite for the porous film.

Figure 7-22 The SEM image and EDX spectrum of the ZnO porous film after sol-gel TiO$_2$ coating treatment.
Figure 7-23. Concentration profiles of estrone solution under UV irradiation without catalyst (black line), with ZnO porous film as catalyst (red line), and with ZnO/TiO$_2$ porous film by sol-gel as catalyst (green line).

The sol-gel prepared ZnO/TiO$_2$ porous films were then tested for photocatalytic activity under UV irradiation together with the ZnO porous film. The test setup was the same as before, and the results are shown in Figure 7-23, exhibiting a similar results as that in Figure 7-19. The catalytic efficiency of these two films are at the same level. The sol-gel prepared ZnO/TiO$_2$ porous film has a slightly better performance, but the difference is not significant.

7.4.1.5 Degradation under Visible Light Irradiation

As discussed before, the other way to examine the effect of TiO$_2$ on the photocatalytic ability of the porous film is eliminating the UV light. Therefore, the photocatalytic activity of ZnO, ZnO/TiO$_2$ by sputtering-wet oxidation and ZnO/TiO$_2$
by sol-gel process were tested under visible light. The visible light was obtained by blocking the UV light of the lamp by using a UV filter (Kenko). Curve (b) in Figure 7-20 shows the light intensity distribution in red at the solution surface when the UV filter is used. Only two small UV peak at 365 nm and 390 nm were left after the blocking, and the short wavelength UV light ($\lambda < 300$ nm) was completely removed. Hence, the photolysis of estrone would not occur in this test.

![Concentration profiles of estrone solution under visible light irradiation without catalyst (black line), with ZnO porous film as catalyst (red line), with porous film ZnO/TiO$_2$ as catalyst (green line), and with porous film ZnO/TiO$_2$ by sol-gel as catalyst (blue line).](image)

The results are summarised in Figure 7-24. Under visible light, the photocatalytic activity of ZnO porous film was reduced. After 4 hr degradation time, about 35% of estrone was degraded by ZnO porous film. On the other hand, the TiO$_2$ containing porous film showed much better photocatalytic performance than
ZnO porous film under the visible light. After 4 hr degradation, 72% estrone was decomposed in the solution with ZnO/TiO$_2$ porous film as the catalyst, and the C/Co value in the solution containing ZnO porous film with sol-gel deposited TiO$_2$ was only around 17%. The higher catalytic activity of the latter one can be attributed to the higher TiO$_2$ content from the sol-gel treatment. These results agree well with the optical properties found by UV-VIS and PL testing.

In summary, both ZnO and ZnO/TiO$_2$ porous films can photo degrade estrone under UV and/or visible light. Their catalytic performance under UV light is similar, but they have bigger differences when under visible light. The TiO$_2$ containing porous film has much higher photocatalytic activity than ZnO porous film under visible light.

### 7.5 Summary

In conclusion, highly porous ZnO composite film has been produced by reactive sputtering Zn target followed by wet oxidation process. It is also demonstrated that co-reactive sputtering TiO$_2$ and Zn targets followed by wet oxidation can produce porous ZnO/TiO$_2$ composite film with anatase TiO$_2$ nano-clusters on the surface. This porous ZnO/TiO$_2$ film shows enhanced PL spectrum in the visible light range from TiO$_2$ which is attributed to the resonant PL effect from the coupling between TiO$_2$ and ZnO. The photocatalytic ability of these porous ZnO and ZnO/TiO$_2$ films has been tested. The results indicate that ZnO and ZnO/TiO$_2$ porous films show similar performance under UV light, while ZnO/TiO$_2$ porous film has better activity under visible light, which is attributed to the high surface area resulted from the porous structure and the formation of TiO$_2$ anatase phase nanostructures on the film surface. Further increasing TiO$_2$ content in the porous film by sol-gel method can also improve the photocatalytic efficiency under visible light.
CHAPTER 8. CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

The work reported in this thesis is mainly focused on the synthesis, characterization, and application of ZnO based low-dimensional nanostructures produced by the wet oxidation method. The following goals have been achieved:

1) A systematically investigation of the influences of various experimental parameters on the formation of ZnO nanostructures, and better understanding of the ZnO nanostructure growth mechanisms in the wet oxidation process.

2) The successful development of two doping methods with the wet oxidation process, and produced Ag doped, N doped, and Ag-N co-doped ZnO nanostructure.

3) The preparation of ZnO and ZnO/TiO₂ composite porous films using wet oxidation.

The influences of various factors, including Zn precursor structures, oxidation temperature and time, water vapour concentration, and O₂ flow-rate, on the growth of ZnO nanostructures have been systematically investigated. It was found that Zn precursors with a deposition time of 5 to 9 min were most favourable for the growth of ZnO nanowires, and the optimum oxidation time and temperature are 4 to 5 hr, and 420°C.

The ZnO nanowire/belt growth mechanism during the wet oxidation process was established based on the experimental results. The growth of ZnO nanowires by wet oxidation is a combined process of water vapour assisted surface diffusion of Zn atoms and vapour-solid (V-S) transformation mechanism. The interaction of water vapour with Zn has major influence on the density and feature of ZnO
nanostructures. The duration of the V-S process has significant effects on the final lengths of the nanowires and nanobelts, as well as on their distribution density.

Doping Ag to the ZnO nanostructure was realized by mixing a small amount of Ag to the Zn precursor film prior to the wet oxidation process. N could be doped to ZnO nanowires by adding NH$_3$ to the oxidation atmosphere. The effectiveness of the doping method was checked by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) measurement. TEM studies showed that Ag doping did not change the growth orientation of the nanowires/belts, and showed concentration gradient of Ag along the nanobelt growth direction. The XPS indicated that the doped Ag was in oxide chemical state in ZnO.

The PL studies showed that the Ag doping enhanced the ZnO ultra-violet (UV) emission of nanowires by more than three times. This could be attributed to the photo-carrier escaping more easily from Ag ions than from Zn ions. In the temperature dependent PL measurement, the Ag:ZnO samples exhibited different behaviour with ZnO.

N:ZnO nanowires were also synthesised by using the wet oxidation process. The O$_2$ was bubbled through NH$_3$ solution instead of deionised water, so that the NH$_3$ was carried into the furnace as N source. By means of scanning electron microscopy (SEM) analysis, the surface morphologies have shown that a high quantity of nanowires could still be produced at 450°C, but not at 600°C. However the introduction of NH$_3$ has hindered the growth of nanowires at 450°C for the pure Zn precursor film. XPS study indicated that at this temperature N had already incorporated into the ZnO lattice, but mainly at the O site in the nitrogen molecule form (N$_2$)$_0$, further annealing was not helpful to give nitrogen atom substituting O site (N$_0$).
While Ag doping prior to the oxidation process could assist the growth of ZnO nanowires in the NH₃/O₂/H₂O atmosphere, both the length and the density of the nanowire increased from the Ag-doped Zn after the thermal treatment at 450°C. Zn₃N₂ nanocrystals could be identified in the Ag-N co-doped nanowires by TEM; and XPS analysis demonstrated that Ag doped Zn had higher Zn-N concentration after the oxidation at 450°C, inferring that Ag assisted the Zn-NH₃ reaction at 450°C. The PL spectrum of the N:ZnO had the peak which had been assigned to the acceptor state originated from N doping. Therefore, the corporation of N into the ZnO has been demonstrated, but the realization of p-type conduction need to be further confirmed by experiment.

Finally, highly porous ZnO composite films have been produced by reactive sputtering Zn target plus wet oxidation method. It has also been found that co-reactive sputtering TiO₂ and Zn targets followed by wet oxidation could produce ZnO/TiO₂ composite porous films. TiO₂ nano-clusters in anatase phase were formed on the surface of the ZnO/TiO₂ porous films after the wet oxidation process. This porous ZnO/TiO₂ films showed enhanced PL spectrum in visible light range, resulting from TiO₂, probably due to the resonant effect with ZnO.

The photocatalysis ability of this porous ZnO and ZnO/TiO₂ films have been tested. ZnO and ZnO/TiO₂ porous films gave a similar performance under UV light, but ZnO/TiO₂ porous film was shown to have better activity under visible light, which was attributed to the high surface area resulted from the porous structure and the formation of TiO₂ anatase phase nanostructures on the film surface. A further increase in the TiO₂ content of the porous film by sol-gel method could also improve the photocatalysis activity under visible light.
8.2 Future Work

Whilst this thesis has addressed a number of issues in the ZnO nanostructure synthesis by wet oxidations, like all investigations there are still many avenues that are deserving of further exploration, although some of them fall outside the scope of this thesis. Future directions related to the work in this thesis are presented below.

Firstly, the Zn precursors used in this thesis were all prepared by magnetron sputtering, which may be an issue from the cost-efficiency point of view. Further studies should be carried out on Zn precursors in other forms, such as Zn foils, Zn films deposited by electrochemical deposition.

Elements other than Ag can be tried as the dopants to ZnO nanowires with the first doping method having been discussed in this thesis. This is mainly usefully for the metallic elements, such as Mg, Al, Mo and cobalt Co. Various dopants may help tune the ZnO nanowires with respect to its electrical, optical and magnetic properties.

In order to check whether the N doping can be improved from the current one, other nitrogen sources such as N₂O, NO and NO₂ can be tried to replace NH₃ in the second doping method.

Direct measurements of the electrical properties of the pure ZnO and doped-ZnO nanowires/nanobelt should be carried out, which will give direction information about the doping effectiveness, and whether or not the doping can induce stable p-type conductivity. This part of work would involve collecting nanowires, electrodes application on the nanowires and micro- and nano- electrical property measurements. Our laboratories are not strong in these aspects.

This thesis has shown that the ZnO and ZnO/TiO₂ porous films have good photocatalysis properties, but their photocatalytic ability should be studied more systemically towards special applications. For example, the effect of film thickness and porosity on the photocatalytic ability; how the photocatalytic ability varies
under different wavelength light, and how the photocatalytic ability changes across different chemicals.

The thick porous films have great potential in the applications including the dye sensitised solar cell (DSSC). Therefore we are conducting tests on the performance of ZnO and ZnO/TiO$_2$ as the electrode materials for DSSC. This is an on-going research that we expect to obtain good results.
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