Synthesis and Characterization of ZnO Nanostructures

Li Li Yang

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Synthesis and characterization of ZnO nanostructures

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Abstract

One-dimensional ZnO nanostructures have great potential applications in the fields of optoelectronic and sensor devices. Therefore, it is very important to realize the controllable growth of one-dimensional ZnO nanostructures and investigate their properties. The main points for this thesis are not only to successfully realize the controllable growth of ZnO nanorods (ZNRs), ZnO nanotubes (ZNTs) and ZnMgO/ZnO heterostructures, but also investigate the structure and optical properties in detail by means of scanning electron microscope (SEM), transmission electron microscope (TEM), resonant Raman spectroscopy (RRS), photoluminescence (PL), time resolved PL (TRPL), X-ray photoelectron spectroscopy (XPS) and Secondary ion mass spectrometry (SIMS).

For ZNRs, on one hand, ZNRs have been successfully synthesized by a two-step chemical bath deposition method on Si substrates. The diameter of ZNRs can be well controlled from 150 nm to 40 nm through adjusting the diameter and density of the ZnO nanoparticles pretreated on the Si substrates. The experimental results indicated that both diameter and density of ZnO nanoparticles on the substrates determined the diameter of ZNRs. But when the density is higher than the critical value of $2.3 \times 10^8$ cm$^{-2}$, the density will become the dominant factor to determine the diameter of ZNRs.

One the other hand, the surface recombination of ZNRs has been investigated in detail. Raman, RRS and PL results help us reveal that the
surface defects play a significant role in the as-grown sample. It is the first time to the best of our knowledge that the Raman measurements can be used to monitor the change of surface defects and deep level defects in the CBD grown ZNRs. Then we utilized TRPL technique, for the first time, to investigate the CBD grown ZNRs with different diameters. The results show that the decay time of the excitons in ZNRs strongly depends on the diameter. The altered decay time is mainly due to the surface recombination process. A thermal treatment under 500°C can strongly suppress the surface recombination channel. A simple carrier and exciton diffusion equation is also used to determine the surface recombination velocity, which results in a value between 1.5 and 4.5 nm/ps. Subsequently, we utilized XPS technique to investigate the surface composition of as-grown and annealed ZNRs so that we can identify the surface recombination centers. The experimental results indicated that the OH and H bonds play the dominant role in facilitating surface recombination but specific chemisorbed oxygen also likely affect the surface recombination. Finally, on the basis of results above, we explored an effective way, i.e. sealing the beaker during the growth process, to effectively suppress the surface recombination of ZNRs and the suppression effect is even better than a 500°C post-thermal treatment.

For ZNTs, the structural and optical properties have been studied in detail. ZNTs have been successfully evolved from ZNRs by a simple chemical etching process. Both temperature-dependent PL and TRPL results not only further testify the coexistence of spatially indirect and direct transitions due to the surface band bending, but also reveal that less nonradiative contribution to the emission process in ZNTs finally causes their strong enhancement of luminescence intensity.

For ZnMgO/ZnO heterostructures, the Zn0.94Mg0.06O/ZnO heterostructures have been deposited on 2 inch sapphire wafer by metal
organic chemical vapor deposition (MOCVD) equipment. PL mapping demonstrates that Mg distribution in the entire wafer is quite uniform with average concentration of ~6%. The annealing effects on the Mg diffusion behaviors in Zn$_{0.94}$Mg$_{0.06}$O/ZnO heterostructures have been investigated by SIMS in detail. All the SIMS depth profiles of Mg element have been fitted by three Gaussian distribution functions. The Mg diffusion coefficient in the as-grown Zn$_{0.94}$Mg$_{0.06}$O layer deposited at 700 °C is two orders of magnitude lower than that of annealing samples, which clearly testifies that the deposited temperature of 700 °C is much more beneficial to grow ZnMgO/ZnO heterostructures or quantum wells.

This thesis not only provides the effective way to fabricate ZNRs, ZNTs and ZnMgO/ZnO heterostructures, but also obtains some beneficial results in aspects of their optical properties, which builds theoretical and experimental foundation for much better understanding fundamental physics and broader applications of low-dimensional ZnO and related structures.

**Keywords:** Zinc oxide; nanostructures; heterostructures; controllable growth; optical properties; postannealing; diffusion coefficient
Preface

Life is never easy, especially for a female who is in the PhD position and far away from her family and homeland. No matter how much love and support she may receive from her family and friends, she always have to depend on her own in the field of scientific research, because that is the purpose of PhD education: reveal and overcome problems. From this point of view, I am so “unlucky” to be one of them as someone says. But in another aspect, I dare to say that it is my huge fortune to have this memorable experience in my life.

For me, being a PhD student is more like climbing a famous high mountain with a fantastic view on the top in a pouring rain day. You know your destination, but you never know what will happen when you get there since the rain and fog is surrounding the mountain. You can either keep going or give up during the entire trip. If you stick to the end, no matter whether you see the fantastic view or not, you will always obtain something, for example, strengthening your willpower. Sooner or later, they will pay your back. I believe they are the real fortune of life, which is the faith to support me to accomplish this work.

When I finish typing the very last word in this thesis, I will be not a student in a university anymore, but a freshman in the society in near future. A brand new door is right there, what should I do is to use a right key to open it. Maybe I already own one. Then a new journey shall begin.
List of publications

Papers included in the thesis:

**Paper I**

Size-controlled growth of well-aligned ZnO nanorod arrays with two-step chemical bath deposition
L.L. Yang, Q.X. Zhao and Magnus Willander

**Paper II**

Effective way to control the size of well-aligned ZnO nanorod arrays with two-step chemical bath deposition
L.L. Yang, Q.X. Zhao, M. Willander, J.H. Yang

**Paper III**

Annealing effects on optical properties of low temperature grown ZnO nanorod arrays
L.L. Yang, Q.X. Zhao, M. Willander, J.H. Yang and I. Ivanov
Journal of Applied Physics, 105 (2009) 053503

**Paper IV**

Surface Recombination in ZnO Nanorods Grown by Chemical Bath Deposition
Q.X. Zhao, L.L. Yang, M. Willander, B. E. Sernelius and P.O. Holtz
Journal of Applied Physics, 104 (2008) 073526
Paper V

Origin of the surface recombination centers in ZnO nanorods arrays by X-ray photoelectron spectroscopy

Paper VI

Effective Suppression of Surface Recombination in ZnO Nanorods Arrays during the Growth Process

Paper VII

Indirect optical transition due to surface band bending in ZnO nanotubes
Submitted

Paper VIII

Mg diffusion in Zn$_{0.94}$Mg$_{0.06}$O/ZnO heterostructures grown by MOCVD
Submitted
Additional papers not included in this thesis

Size dependent carrier recombination in ZnO nanocrystals
Galia Pozina, Lili Yang, Qingxiang Zhao, Lars Hultman, and Pavlos Lagoudakis
Manuscript

Trimming of aqueous chemically grown ZnO nanorods into ZnO nanotubes and their comparative optical properties

Bending flexibility, kinking and buckling characterization of ZnO nanorods/nanowires grown on different substrates by high and low temperature methods
M. Riaz, A. Ful, L. L. Yang, O. Nur, M. Willander, and P. Klason
Journal of Applied Physics, 104 (2008) 104306

Zinc oxide nanorod based photonic devices: recent progress in growth, light emitting diodes and lasers.

Zinc oxide nanowires: controlled low temperature growth and some electrochemical and optical devices
ZnO nanowires: chemical growth, electrodeposition, and application to intracellular nano-sensors
M. Willander, P. Klason, L. L. Yang, Safaa M. Al-Hilli, Q. X. Zhao, O. Nur

Light-emitting diodes based on n-ZnO nano-wires and p-type organic semiconductors
M. Willander, A. Wadeasa, P. Klason, L. L. Yang, S. Lubana Beegum, S. Raja, Q.X. Zhao, O. Nur
Proceedings of the SPIE - The International Society for Optical Engineering, 6895 (2008) 68950O-1-10 (Invited)

Investigation on the surface recombination of ZnO nanorods arrays
Lili Yang, Qingxiang Zhao, Magnus Willander

Surface Recombination in ZnO Nanorods Grown by Aqueous Chemical Method
Q.X. Zhao, L.L. Yang, M. Willander, G. Pozina and P.O. Holtz
The 29th International Conference on the Physics of Semiconductors, 27/7-1/8 2008 in Rio De Janero, Brazil.

Light emitting didoes based on n-ZnO nanowires and p-type organic semiconductors
M. Willander, A. Wadeasa, Lili Yang, Q.X.Zhao, and O. Nur
Photonic West, Integrated Optoelectronic Devices Symposium, San Jose California, January (2008)

L.L. Yang, Q.X. Zhao and M. Willander
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At the moment when I just finished typing the very last word in this thesis, a kind of release suddenly came out from my bottom heart and run through entire body. All the scenes happened within last three and a half years in Linköping University are suddenly flashing back. Many people who ever contributed to the work and helped me in the life slowly came into my mind one by one. I truly appreciate and cherish what all of you have done for me, even though my gratitude is beyond words.

First of all, I would like to express my sincere appreciate to my main supervisor Associate Prof. Qingxiang Zhao, co-supervisor Prof. Magnus Willander and Prof. Jinghai Yang in China who provides this huge opportunity for me and brings me into this warm family, our physical electronics group. Therefore, I have a chance to have a brilliant new life in Sweden which I will never forget for my entire life.

I would like to express my gratitude to my main supervisor Qingxiang Zhao again for your patient guide and tutor in the whole research work and kind help for my daily life in Sweden. Without your support and input this thesis would not have been completed so fast. Particularly, with your immense knowledge, you help me open a new door when I only have a small window to look into the physics world. It is my honor to be your student and I am really proud of it.

I would also like to thank my co-supervisor Prof. Magnus Willander again for your guide, help, encouragement, support and trust all the times. You keep working so hard to create the great research environment for
our group and so kind to do your best to support your students for their future. What you do will always remind me how to become a good teacher and even a great group leader if I have that chance in my future.

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For my parents and younger sister, words are not enough to express my gratitude for you. Without your selfless love and endless support, I can not be me today. Thank you for always being there.

Last but not least, my dear husband Helei Lu, deeply thanks for love, support and everything you have done for me. Thank you so much.

Lili Yang
Norrköping 2010-8-16
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Chapter 1
Introduction

Nowadays, the products of semiconductor industry spread all over the world and deeply penetrate into the daily life of human being. The starting point of semiconductor industry was the invention of the first semiconductor transistor at Bell Lab in 1947. Since then, the semiconductor industry has kept growing enormously. In the 1970’s, the information age of human being was started on the basis of the stepwise appearance of quartz optical fiber, III-V compound semiconductors and gallium arsenide (GaAs) lasers. During the development of the information age, silicon (Si) keeps the dominant place on the commercial market, which is used to fabricate the discrete devices and integrated circuits for computing, data storage and communication. Since Si has an indirect band gap which is not suitable for optoelectronic devices such as light emitting diodes (LED) and laser diodes, GaAs with direct band gap stands out and fills the blank for this application. As the development of information technologies, the requirement of ultraviolet (UV)/blue light emitter applications became stronger and stronger which is beyond the limits of GaAs. Therefore, the wide bandgap semiconductors such as SiC, GaN and ZnO, i.e. the third generation semiconductors, come forth and turn into the research focus in the field of semiconductor.

ZnO is a typical II-VI semiconductor material with a wide bandgap of 3.37 eV at room temperature. Although its bandgap value is closer to
GaN (3.44 eV), its exciton binding energy is as higher as 60 meV, which is much larger than that of GaN (21 meV) and even room temperature thermal excited energy (25 meV). Therefore, theoretically, we can harvest high efficient UV exciton emission and laser at room temperature, which will strongly prompt the applications of UV laser in the fields of benthal detection, communication and optical memory with magnitude enhancement in the performance. Moreover, the melting point of ZnO is 1975 °C, which determines its high thermal and chemical stability. Plus, ZnO has owned a huge potentially commercial value due to its cheaper price, abundant resources in the nature, environment-friendly, simply fabrication process and so on. Therefore, ZnO has turned into a new hot focus in the field of short-wavelength laser and optoelectronic devices in succession to GaN in the past decade.

In fact, the research interest in ZnO has waxed and waned over the years. The first enthusiasm started studies of the lattice parameter by M.L. Fuller in 1929 [1] and C.W.Bunn in 1935[2], but the enthusiasm flagged with the difficulty in producing p-type doping and high quality crystal crystalline material. Until 1997, Tang at al reported, for the first time, the room-temperature ultraviolet (UV) laser emission from self-assembled ZnO microcrystallite thin films [3,4]. They utilized laser molecular beam epitaxy to grow ZnO thin film with alveolate structures on the sapphire substrates. After a excitation by the frequency-tripled output (355 nm) from a pulsed Nd:YAG laser, a room temperature UV stimulated emission located at 400 nm can be observed. It is even shorter than that from GaN, which will further improve the density of data storage and recording speed of optical communication. As compared to commercial GaAs laser used in the market, the recording data capacity with ZnO laser can be enhanced about 4 times with much faster speed. Subsequently, R.F. Service remarked on their results in Science as a great work and a cool
way to beat the blues. Since then, a great revolution caused by ZnO in the field of semiconductors has been started. The number of articles published on ZnO has been increasing every year and in 2007 ZnO becomes the second most popular semiconductor materials after Si. On one hand, the popularity to a large extent is due to the improvements in growth of high quality, single crystalline ZnO in both epitaxial layers and bulk form. On the other hand, especially since the emergence of the nanotechnology, novel electrical, mechanical, chemical and optical properties are introduced with the reduction in size, which are largely believed to be the result of surface and quantum confinement effects. Study of one dimensional (1D) materials has become a leading edge in nanoscience and nanotechnology.

ZnO is a versatile functional material. 1D ZnO nanostructures such as nanotubes [5-12], nanowires [13,14], nanorods [14], nanobelts [15,16], tetrapods [17] and nanoribbons [18] stimulate considerable interests for scientific research due to their importance in fundamental physics studies and their potential applications in nanoelectronics, nanomechanics, and flat panel displays. Particularly, the optoelectronic device application of 1D ZnO nanostructure becomes one of the major focuses in recent nanoscience researches [13,19-21].

During the last decade, ZnO epilayer and various ZnO nanostructures have been grown by various techniques. A major advantage for ZnO nanostructures, e.g. nanorods and nanotubes, is that they can be easily grown on various substrates and non-lattice materials including flexible polymers. In addition, ZnO nanostructures can be advantageous with a low density of defects. The growth of defect-free structures is more likely for nanostructures in comparison with epilayers, since the strain in the nanostructures can be efficiently relieved by
elastic relaxation at the free lateral surfaces rather than by plastic relaxation.

In order to utilize the applications of nanostructure materials, it usually requires that the crystalline morphology, orientation and surface architecture of nanostructures can be well controlled during the preparation processes. As concerned as ZnO nanostructures, although different fabrication methods, such as vapor-phase transport [22-24], pulsed laser deposition [25], chemical vapor deposition [26,27] and electrochemical deposition [6], have been widely used to prepare ZnO nanostructures, the complex processes, sophisticated equipment and high temperatures make them very hard to large-scale produce for commercial application. On the contrary, aqueous chemical method shows its great advantages due to much easier operation and very low growth temperature (95°C) [14, 28], in addition to low cost. However, the ZnO nanostructures grown by this method show a poor reproducibility, difficulty to control size and bad orientation, particularly on substrates (such as Si) with large lattice mismatch and different crystalline structures in comparison with ZnO. Hence, it is still a significant challenge to obtain controllable growth of ZnO nanostructures (i.e. nanorods and nanotubes).

In terms of application of ZnO nanostructures, it requires not only that their crystalline morphology, orientation and surface architecture be well controlled during the preparation processes, but also an improved quality of their optical and electronic properties. Unfortunately, ZnO nanostructures, such as nanorods and nanotubes, grown at relatively low temperature usually showed poor crystallization and optical properties. In addition, one of the significant differences between ZnO nanostructures and an epilayer is the larger surface area of the former. This large surface area can be an advantage for some applications, for example sensor
devices. However, it can also be a problem in other applications, for example, optoelectronic devices such as light emitting diodes and solar-cell devices, since the surface recombination rate may become dominating, resulting in a short carrier life time. So far, the knowledge about surface recombination or other surface effects in ZnO nanostructures is still limited, which is necessary and urgent to be investigated.

In the case of ZnO epitaxial layer, on one hand, it is well known that an important issue for designing ZnO-based optoelectronic devices is the realization of band gap engineering so that people can create barrier layers and quantum well in the heterojunction devices [29]. A key technology to realize band gap engineering is to introduce appropriate metal element to synthesize the ternary compounds [30], such as ZnCdO[31,32] ZnMgO[33] and ZnBeO[34,35]. In these alloys, the band gap has been successfully tuned between 2.99 and 5.3 eV[34,36]. In addition, heterostructures [37] and quantum wells [38] have also been realized, proving the feasibility of ZnO based optoelectronic devices. Among these ternary compounds, ZnMgO alloy has attracted more attention and apparently becomes the focus in recent years due to the similarity in ionic radii between Zn$^{2+}$ (0.74Å) and Mg$^{2+}$ (0.71Å) which allows for the substitution of magnesium within the wurtzite ZnO lattice[39]. Plus, higher luminescence efficiency can still be achieved for higher Mg composition of ZnMgO alloys, which strongly indicates that ZnMgO has great potential for use in UV region optoelectronic devices [40]. So far, up to 33% solid solubility of MgO in ZnO has been reported for thin-film alloys with wurtzite type structure [41]. The fundamental bandgap energy of ZnMgO is mainly depended on the alloy composition, which has been realized the modulation from 3.37 to 4.0 eV [42]. However, due to the different lattice symmetries of ZnO (wurtzite) and MgO (rocksalt), the
growth process and mechanism of ZnMgO is complicated [29]. Poor crystalline quality and phase separation are the main problems that we have to overcome for the practical application. Therefore, the growth of ZnMgO epitaxial layers is essential for the bandgap engineering as well as device application, especially for fabricating the heterostructures and quantum well.

On the other hand, usually, the ZnMgO are grown at relative higher temperature in order to achieve epitaxial layers with good crystal quality. Or in another way, a post-deposition annealing process is carried out on a as-grown ZnMgO epitaxial layer to improve its crystalline perfection and increase conductivity [43]. It is well known that the post-thermal treatment will induce the diffusion of Mg elements in the ZnMgO epitaxial layer. Of course, this high-temperature deposition or post-thermal treatment has no harm to ZnMgO epitaxial layers. But for ZnMgO/ZnO heterostructures and quantum well, it is well known that the high-temperature deposition or post-thermal treatment will induce the diffusion of Mg elements in them. This interdiffusion between the layers caused by high-temperature growth or post-thermal processing will broaden the interfaces, which can bring a strong impact on their properties or even worse result in the failed formation of structures. Thus, what extend of the thermal-induced diffusion of Mg is a key parameter in the synthesis of ZnMgO/ZnO heterostructures and quantum well. It is obvious that ZnMgO/ZnO heterostructure is a very good candidate to get the diffusion information due to its simple structure. However, so far, the investigation of Mg diffusion in the ZnMgO/ZnO heterostructure is still limited. Therefore, the corresponding systemic investigation is necessary and significant for not only fabrication but practical application.

Above, the background and the problems for ZnO nanostructures and ZnMgO epitaxial layer were briefly reviewed. This thesis will be
focused on three types of ZnO structures, i.e. ZnO nanorods (ZNRs), ZnO nanotubes (ZNTs) and ZnMgO epitaxial layers.

For ZNRs, I mainly expand on four topics. The first topic is how to realize the size controllable growth of ZNRs with chemical bath deposition (CBD) method (Paper I and II); the second one is the investigation of the surface recombination behaviour of ZNRs (Paper III and IV); the third one is the determination of surface recombination centers in ZNRs (Paper V); the forth one is how to suppress the surface recombination, especially during the growth progress, in order to improve the optical properties (Paper VI).

For ZNTs, I only focus on their temperature-dependent optical properties, which clearly reveals the existence of spatially indirect optical transition in the emission process due to the surface band bending effect (Paper VII).

For ZnMgO/ZnO heterostructures, I utilize metal organic chemical vapor deposition (MOCVD) to fabricate the samples. Then the annealing effects on the Mg diffusion behaviours in the ZnMgO/ZnO heterostructures have been investigated in detail by secondary ion mass spectrometry (SIMS) measurement to perfect the synthesized conditions (Paper VIII).

For the first five chapters in the thesis give a brief review of ZnO properties and our experimental details. In Chapter 2, the basic properties of ZnO are introduced. Chapter 3 describes the synthesis of ZNRs, ZNTs and ZnMgO/ZnO heterostructures. Chapter 4 introduces the experimental details used for this work. Finally, the thesis ends with some concluding remarks and outlooks for the future in Chapter 5.
Chapter 2

Structural and Optical Properties of ZnO

ZnO is a key technological material. ZnO is a wide band-gap (3.37 eV) compound semiconductor that is suitable for short wavelength optoelectronic applications. The high exciton binding energy (60meV) in ZnO crystal can ensure efficient excitonic emission at room temperature and room temperature ultraviolet (UV) luminescence has been reported in nanowires and thin films [3, 4, 13]. In addition, the lack of a centre of symmetry in wurtzite, combined with large electromechanical coupling, results in strong piezoelectric and pyroelectric properties and the consequent use of ZnO in mechanical actuators and piezoelectric sensors [44-48]. Furthermore, ZnO is a versatile functional material that has a diverse group of growth morphologies, such as nanotubes [5-12], nanowires [13,14], nanorods [14], nanobelts [15,16], tetrapods [17], nanoribbons [18], nanorings [49], nanopropeller [50], nanocombs [51-53] and nanocages [54]. These ZnO nanostructures are easily formed even on cheap substrates such as glass and hence they have a promising potential in the nanotechnology future. Finally, ZnO nanostructures are also attractive for sensor and biomedical application due to its bio-safety and large surface area [55-59]. As well as we know, all these applications definitely originate from its basic properties. Therefore, in order to in-depth know about ZnO, the structural and optical properties of ZnO will be introduced in detail in this chapter.
2.1 Crystal and surface structure of ZnO

At ambient pressure and temperature, ZnO crystallizes in the wurtzite (B4 type) structure, as shown in figure 2.1[60]. This is a hexagonal lattice, belonging to the space group P63mc with lattice parameters $a = 0.3296$ and $c = 0.52065$ nm. Usually, we can treat it as a number of two type planes, i.e. tetrahedrally coordinated $O^{2-}$ and $Zn^{2+}$ ions, stacked alternately along the c-axis (Figure 2.1). Or in another way, it also can be characterized by two interconnecting sublattices of $Zn^{2+}$ and $O^{2-}$, such that each Zn ion is surrounded by a tetrahedra of O ions, and vice-versa. No a doubt, this kind of tetrahedral coordination in ZnO will form a noncentral symmetric structure with polar symmetry along the hexagonal axis, which not only directly induces the characteristic piezoelectricity and spontaneous polarization, but also plays a key factor in crystal growth, etching and defect generation of ZnO.

Figure 2.1: The wurtzite structure model of ZnO. The tetrahedral coordination of Zn-O is shown [Reprinted with permission from Ref.[60], Copyright 2004 by IOP Publishing Ltd.].
The polar surface is another important characteristic of ZnO structure. As well as we known, wurtzite ZnO crystallizes do not have a center of inversion. If the ZnO crystals such as nanorods and nanotubes grow along the c axis, two different polar surfaces will be formed on the opposite sides of the crystal due to the suddenly termination of the structure, i.e. the terminated Zn-(0001) surface with Zn cation outermost and the terminated O-(0001) surface with O anion outermost. Naturally, these positively charged Zn-(0001) and negatively charged O-(0001) surfaces are the most common polar surfaces in ZnO, which subsequently results in a normal dipole-moment and spontaneous polarization along the c-axis as well as a divergence in surface energy. Generally, the polar surfaces have facets or exhibit massive surface reconstructions in order to maintain a stable structure. However, ZnO± (0001) are exceptions: they are atomically flat, stable and without reconstruction [60-63]. Efforts to understand the superior stability of the ZnO ± (0001) polar surfaces are at the forefront of research in today’s surface physics [64–67]. Besides these two polar surfaces, The other two most commonly observed facets for ZnO are {2 1 1 0} and {0 1 1 0}, which are non-polar surfaces with an equal number of Zn and O atoms. They have lower energy than the {0001} facets.

In addition to the wurtzite phase, ZnO is also known to crystallize in the cubic zincblende and rocksalt (NaCl) structures, which are illustrated in figure 2.2 [61]. Zincblende ZnO is stable only by growth on cubic structures [68–70], while the rocksalt structure is a high-pressure metastable phase forming at ~10 GPa, and cannot be epitaxially stabilized [71]. Theoretical calculations indicate that a fourth phase, cubic cesium chloride, may be possible at extremely high temperatures, however, this phase has yet to be experimentally observed [72].
2.2 Basic physical parameters for ZnO

Table 2.1 shows a compilation of basic physical parameters for ZnO [73, 74]. It should be noted that there still exists uncertainty in some of these values. For example, there have few reports of p-type ZnO and therefore the hole mobility and effective mass are still in debate. Similarly, the values for thermal conductivity show some spread in values and this may be a result of the influence of defects such as dislocations [75], as was the case for GaN. The values for carrier mobility will undoubtedly increase as more control is gained over compensation and defects in the material.
Table 2.1: Physical parameters of ZnO

<table>
<thead>
<tr>
<th>Physical parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters at 300 K</td>
<td></td>
</tr>
<tr>
<td>$a_0$</td>
<td>0.32495 nm</td>
</tr>
<tr>
<td>$c_0$</td>
<td>0.52069 nm</td>
</tr>
<tr>
<td>$a_0/c_0$</td>
<td>1.602 (ideal hexagonal structure shows 1.633)</td>
</tr>
<tr>
<td>$U$</td>
<td>0.345</td>
</tr>
<tr>
<td>Density</td>
<td>5.606 g/cm$^3$</td>
</tr>
<tr>
<td>Stable phase at 300 K</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>Melting point</td>
<td>1975°C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.6, 1–1.2</td>
</tr>
<tr>
<td>Linear expansion coefficient (°C)</td>
<td>$a_0$: 6.5 $\times$ 10$^{-6}$</td>
</tr>
<tr>
<td></td>
<td>$c_0$: 3.0 $\times$ 10$^{-6}$</td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>8.656</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.008, 2.029</td>
</tr>
<tr>
<td>Energy gap</td>
<td>3.37 eV, direct</td>
</tr>
<tr>
<td>Energy gap</td>
<td>$&lt;10^6$ cm$^3$ (max n-type doping $&gt;10^{20}$ cm$^3$ electrons; max p-type doping $&lt;10^{17}$ cm$^3$ holes)</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>60 meV</td>
</tr>
<tr>
<td>Electrons 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>
</tbody>
</table>
2.3 Electronic band structure

It is well known that the band structure of a given semiconductor is pivotal in determining its potential utility. Thus, an accurate knowledge about the band structure of a semiconductor is quite critical for exploring its applications and even improving the performance. As well as we know, optical measurements and band-structure calculations indeed complement and interdepend on each other for understanding electronic band structures in semiconductors[76]. Since both conduction and valence bands contribute significantly to the energy range where the optical excitations fall in, it is impossible to give a detailed interpretation of optical reflectance without at least a semiquantitative band-structure calculation first. In like manner, the reliability of these calculations in turn depends on the correct interpretation of certain key features in the optical data. Obviously, the process of determining band structure is one of trial and error, but it often leads to a consistent, quantitative, detailed picture of the band structure of semiconductors in a limited range of energy around the fundamental gap.

To date, several theoretical approaches of varying degrees of complexity, such as Green’s functional method [77], Local Density Approximation (LDA) [78-79], GW approximation (GWA) [80, 81] and First-principles (FP) [82-84], have been employed to calculate the band structure of wurtzite ZnO. Besides, a number of experimental data have also been published regarding the band structure of the electronic states in wurtzite ZnO[76, 85-89].

In the aspect of theoretical calculation, the first calculation about energy band of ZnO can be casted back to 1970’s. In 1969, for the first time, U. Rössler calculated the energy bands for hexagonal ZnO along the main symmetry axes of the hexagonal Brillouin zone by Green’s function
method with the relativistic mass velocity and Darwin correction considered [77]. The results showed that the band structures of ZnO differs from the ZnS band structure in that \( d \) bands occur closely below the upper valence bands, and \( p \)-like conduction bands lie 17 eV above the valence bands. Thus, the ZnO band structure exhibits a very broad lowest conduction band. Since then, several more methods such as LDA, WPA and FP had been invented and constantly improved to theoretically calculate the ZnO energy band [78-84]. For example, D. Vogel et al further improved the LDA method by incorporating atomic self-interaction corrected pseudopotentials (SIC-PP), in which Zn 3\( d \) electrons had been accurately taken into account to calculate the electronic band structure of ZnO [78]. The corresponding results have been shown in figure 2.3. On one hand, 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. On the other hand, the band gap as determined from the standard LDA calculations is only \(~3\) eV, as shown in the left panel of figure 2.3. This shrunk band gap was obtained because 3d states have been treated as core levels in order to simplify the calculations in the standard LDA method. According to the calculation results from SIC-PP method as shown in the right panel of figure 2.3, the bottom 10 bands (occurring around -9 eV) correspond to Zn 3\( d \) levels. The next 6 bands from -5 eV to 0 eV correspond to O 2\( p \) bonding states. The first two conduction band states are strongly Zn localized and correspond to empty Zn 3\( s \) levels. In contrast to the left panel, the \( d \)-bands are shifted down in energy considerably and concomitantly the gap is opened drastically. In addition, the dispersion and bandwidth of the O 2\( p \) valence bands are changed significantly. The gap energy and the d-band position are grossly improved as compared to
the standard LDA results. The band gap as determined from this calculation is 3.77 eV, which correlates reasonably well with the experimental value of 3.4 eV. Therefore, we can see that the band gap energy and d-band position have been significantly improved as compared to the standard LDA results.

As early as 1970, D.W. Langer and C. J. Vesely used the x-ray induced photoemission measurement to determine the energy levels of core electrons in ZnO [85]. In 1971, R. A. Powell et al carried out uv photoemission measurements on hexagonal ZnO cleaved in vacuum [76]. The results indicated that the Zn 3d core level located at 7.5±0.2 eV below the valence-band maximum, which was ~3 eV lower than
predicted by Rössler’s Green’s function band calculation [61]. But this assignment is in excellent agreement with the result (7.6 eV) of previous x-ray photoemission measurements [85]. Subsequently, in 1974, L. Ley at al presented the total valence-band x-ray photoemission spectra of 14 semiconductors including the hexagonal ZnO[86]. The results strongly proved that band-structure calculations in combination with x-ray photoemission spectra provide a powerful approach to establishing the total valence-band structure of semiconductors. Until now, some groups still used X-ray photoemission spectroscopy to investigate the band structure of ZnO [87-89].

So far, the coherence between theoretical calculation and experiments for energy band structure has already been reached for a great number of semiconductors, including ZnO of course, since excellent and detailed optical data has been available in many cases.

![Band structure and symmetries of hexagonal ZnO. The splitting into three valence bands (A, B, C) is caused by crystal field and spin-orbit splitting. [Reprinted with permission from Ref.[90], Copyright 2004 by WILEY-VCH Verlag GmbH & Co.].](image-url)
In addition, it is also worth to know that the ZnO valence band is split experimentally by crystal field and spin orbit interaction into three states named A, B and C under the wurtzite symmetry. This splitting is schematically illustrated in Figure 2.4. The A and C subbands are known to possess $\Gamma_7$ symmetry, whilst the middle band, B, has $\Gamma_9$ symmetry [90]. The band gap has the temperature dependence up to 300K given by the relationship:

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

These properties of ZnO give rise to interesting optical properties which will be discussed in following part.

### 2.4 Optical Properties of ZnO

Actually, the investigation about optical properties of ZnO as well as its refractive has been lasted out with a quite long history. The first study started many decades ago, which was around 1960’s [91-109]. The renewed interest in ZnO is fuelled and fanned by its prospects in optoelectronics applications owing to its direct wide band gap of 3.37 eV at room temperature with large exciton energy of 60 meV and efficient radiative recombination. The strong exciton binding energy, which is much larger than that of GaN (25 meV), and the thermal energy at room temperature (25 meV) can ensure an efficient exciton emission at room temperature under low excitation energy. As a consequence, ZnO is recognized as a promising photonic material in the blue-UV region.

As well as we known, the optical properties of ZnO contain a lot of information, such as optical absorption, transmission, reflection, photoluminescence and so on. In this section, I only focus on the
introduction of photoluminescence property since it is the main object I am going to present in this thesis. Firstly, a review on the optical properties of a semiconductor is given first. Secondly, the UV emission and origins of deep level emission band (DLE) in ZnO photoluminescence (PL) spectra are briefly discussed. Thirdly, the surface recombination is introduced in detail. Finally, the surface band bending effect is discussed since usually ZnO nanostructures have a quite large surface-volume ratio.

2.4.1 Optical properties of semiconductor

Both intrinsic and extrinsic effects contribute to the optical properties of a semiconductor [110, 111]. The transitions between the electrons in conduction band and holes in valence band are usually treated as intrinsic optical transitions, in which the excitonic effects due to the Coulomb interaction are also included. Extrinsic properties are related to the electronic states created in the bandgap by dopants/impurities or point defects and complexes, which usually influence both optical absorption and emission processes. The excitons can be bound to neutral or charged donors and acceptors, called bound excitons. The electronic states of these bound excitons strongly depend on the semiconductor material, in particular the band structure. For a shallow neutral donor bound exciton, for example, the two electrons in the bound exciton state are assumed to pair off into a two-electron state with zero spin. The additional hole is then weakly bound in the net hole-attractive Coulomb potential set up by this bound two-electron aggregate. Similarly, neutral shallow acceptor bound excitons are expected to have a two-hole state derived from the topmost valence band and one electron interaction. Other extrinsic
transitions could be seen in optical spectra such as free-to-bound (electron-acceptor) and bound-to-bound (donor-acceptor).

2.4.2 Photoluminescence properties of ZnO

It is well known that at room temperature the PL spectrum from ZnO typically consists of a UV emission band and a broad emission band, as shown in Figure 2.5. At room temperature, The UV emission band is related to a near band-edge transition of ZnO, namely, the recombination of the free excitons. The broad emission band literally between 420 nm and 700 nm observed nearly in all samples regardless of growth conditions is called deep level emission band (DLE). The DLE band has previously been attributed to several defects in the crystal structure such as O-vacancy (V_O) [112-114], Zn-vacancy (V_Zn)[115-117], O-interstitial (O_i) [118], Zn-interstitial (Zn_i) [119], and extrinsic impurities such as substitutional Cu [120]. Recently, this deep level emission band had been

![Figure 2.5: PL spectrum of ZnO nanorods from the sample grown on a 1.7 nm thick Au-layer deposited (001) Si substrate at 890 °C, measured at room temperature with excitation power of 5 mW, the excitation wavelength is 350 nm.](image)
identified and at least two different defect origins ($V_O$ and $V_{Zn}$) with different optical characteristics were claimed to contribute to this deep level emission band [121-123].

At low cryogenic temperatures, bound exciton emission is the dominant radiative channel. Figure 2.6 shows a typical photoluminescence spectrum of $n$-type bulk ZnO measured at 4.2 K [124]. The luminescence spectrum from ZnO extends from the band edge to the green/orange spectral range. Very common is a broad band centered about 2.45 eV extending from the blue into the green range. The lines dominating the spectrum originate from bound exciton (BE) recombinations (excitons bound to neutral donors ($D_0X$) and/or acceptors ($A_0X$)) followed by longitudinal optical (LO) phonon replicas with an energy separation of 72 meV. The free exciton emission with the A-valence band (FXA) positioned at 3.375 eV can already be seen. And a donor-acceptor-pair (DAP) transition around 3.22 eV is found, which is again followed by phonon replicas.

Figure 2.6: Photoluminescence spectrum of bulk ZnO showing excitonic, donor acceptor pair (DAP) and deep level emission. The corresponding phonon replicas with longitudinal optical phonons (LO) are indicated (He-Cd excitation). [Reprinted with permission from Ref.[124], Copyright 2004 by WILEY-VCH Verlag GmbH & Co.]
Table 2.2: Free and bound exciton recombinations and related properties [Reprinted with permission from Ref.[124], Copyright 2004 by WILEY-VCH Verlag GmbH & Co.].

<table>
<thead>
<tr>
<th>line</th>
<th>wavelength (nm)</th>
<th>energy (eV)</th>
<th>localisation energy (meV)</th>
<th>two-electron satellite separation (2P0 - 1S) (meV)</th>
<th>donor binding energy (meV)</th>
<th>chemical identity</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_L</td>
<td>367.72</td>
<td>3.3772</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A_T</td>
<td>367.76</td>
<td>3.3759</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I_0</td>
<td>367.63</td>
<td>3.3725</td>
<td>3.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I_1</td>
<td>367.71</td>
<td>3.3718</td>
<td>4.1</td>
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<tr>
<td>I_m</td>
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<td>3.3679</td>
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<td>I_1'</td>
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<td>3.3674</td>
<td>8.5</td>
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<td>368.29</td>
<td>3.3665</td>
<td>9.4</td>
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<td></td>
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<td>3.3660</td>
<td>9.9</td>
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<tr>
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<td>368.34</td>
<td>3.3628</td>
<td>13.1</td>
<td>34.1</td>
<td>46.1</td>
<td>H</td>
</tr>
<tr>
<td>I_5</td>
<td>368.86</td>
<td>3.3614</td>
<td>14.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I_m</td>
<td>368.92</td>
<td>3.3608</td>
<td>15.1</td>
<td>38.8</td>
<td>51.55</td>
<td>Al</td>
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<tr>
<td>I_m</td>
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<td>3.3604</td>
<td>15.5</td>
<td>40.4</td>
<td>53</td>
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</tr>
<tr>
<td>I_7</td>
<td>369.01</td>
<td>3.3600</td>
<td>15.9</td>
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<tr>
<td>I_8</td>
<td>369.03</td>
<td>3.3598</td>
<td>16.1</td>
<td>42.1</td>
<td>54.6</td>
<td>Ga</td>
</tr>
<tr>
<td>I_m</td>
<td>369.08</td>
<td>3.3593</td>
<td>16.6</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>I_9</td>
<td>369.37</td>
<td>3.3567</td>
<td>19.2</td>
<td>50.6</td>
<td>63.2</td>
<td>In</td>
</tr>
<tr>
<td>I_m</td>
<td>369.76</td>
<td>3.3531</td>
<td>22.8</td>
<td>60.2</td>
<td>72.6</td>
<td></td>
</tr>
<tr>
<td>I_11</td>
<td>370.28</td>
<td>3.3484</td>
<td>27.5</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

* A_L and A_T are the longitudinal and transversal free A-exciton states. A_T is the reference for the determination of the bound exciton localisation energy.

** I_2 and I_3 are assigned to ionised donor bound exciton recombinations.

Until now, up to eleven excitonic recombinations where excitons bind to neutral donors and/or acceptors have been observed [125-129]. The positions of these eleven prominent PL lines are listed in Table 2.2. However, the chemical nature of the donor and acceptor species still remains unclear.

2.4.3 Surface recombination

There are two basic recombination mechanisms in semiconductors, namely radiative recombination and non-radiative recombination. In a radiative recombination event, one photon with energy equal to or near the bandgap energy of the semiconductor is emitted, as illustrated in
Figure 2.7[130]. During non-radiative recombination, the electron energy is converted to vibrational energy of lattice atoms, i.e. phonons. Thus, the electron energy is converted to heat. For obvious reasons, we want the contribution from the non-radiative recombination in light-emitting devices as less as possible.

There are mainly three physical mechanisms by which non-radiative recombination can occur, i.e. (1) non-radiative via deep level; (2) Auger recombination; (3) Surface recombination. We will introduce them individually.

(i) Non-radiative via deep level

Non-radiative recombination is mostly originated from the defects in the crystal structure, such as impurities, native defects, dislocations, and any complexes of defects. In compound semiconductors, the so-called native defects include interstitials, vacancies, and antisite defects. It is quite common for such defects to form one or several energy levels within the forbidden gap of the semiconductor. For instance, the calculated defect energy levels in ZnO from different literature sources
Figure 2.8 The calculated defect energy levels in ZnO from different literature sources. The data marked with the subscript a, b and c respectively originates from Ref. [131], Ref. [132] and Ref. [133]. [Reprinted with permission from Ref.[134], Copyright © 2009 Inderscience Enterprises Ltd.]

are illustrated in Figure 2.8. These levels contribute to radiative or nonradiative recombination. Energy levels within the gap of the semiconductor are efficient recombination centers; in particular, if the energy level is close to the middle of the gap. Those deep levels or traps which promote the non-radiative process are called luminescence killers. The recombination of carriers via such trap levels is shown schematically in Figure 2.9 (a).

Figure 2.9: Band diagram illustrating recombination: (a) non-radiative via deep level; (b) non-radiative via Auger process and (c) radiative [Reprinted with permission from Ref.[130], Copyright 2006 by Cambridge University press].

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(ii) **Auger recombination**

The energy is given to a third carrier, which is excited to a higher energy level without moving to another energy band. After the interaction, the third carrier normally loses its excess energy to thermal vibrations. The recombination of carriers via Auger process is shown schematically in Figure 2.9 (b). Since this process is a three-particle interaction, it is normally only significant in non-equilibrium conditions when the carrier density is very high. The Auger generation process is not easily produced, because the third particle would have to begin the process in the unstable high-energy state.

(iii) **Surface recombination**

From a structural point view, compared with the bulk part of a material, the surface structure is totally different since the crystal growth has been suddenly terminated. That is to say, the periodicity of a crystal lattice is strongly perturbed by the surface. It is well known that the band diagram model is based on the strict periodicity of a lattice. So it is certain that the band structure will be modified by the surface due to the periodicity ending. As a result, some additional electronic states will be formed within the forbidden gap in the semiconductor, which will act as nonradiative centers to strongly suppress the luminescent efficiency and intensity of the materials.

We can also understand the formation of these additional electronic states from a chemical point view. Obviously, the atoms at the semiconductor surface cannot have the same bonding structure as bulk atoms due to the lack of neighboring atoms. Thus, so-called dangling bonds will be formed since some of the valence orbitals can only be partially filled without forming a chemical bond. These dangling bonds, i.e. partially filled electron orbitals, provide electronic states that can be
located in the forbidden gap of the semiconductor. These states can be clarified into acceptor-like or donor-like states, which only depend on the charge state of the valence orbitals. Usually, these dangling bonds do not stand there steadily. They are apt to rearrange themselves to make the surface reconstructions happen probably in three ways. (1) The dangling bonds may also rearrange themselves to form bonds between neighboring atoms in the same surface plane; (2) The atoms in the surface may move into new equilibrium positions that provide higher symmetry or greater overlap of available bonding orbitals [135]; (3) The dangling bonds may absorb the chemical groups from the extrinsic environment to build the new bonds. No matter which kind of rearrangement, these surface reconstructions can produce a locally new atomic structure with different state energies as compared to the bulk atomic states.

It is well known that surface recombination through surface/interface states is a major loss mechanism for photo-generated carriers, and its negative influence on the photonic devices will become stronger as the geometrical dimension of materials is reduced. However, one of the significant differences between nanostructures and an epilayer is the larger surface-to-volume ratio of the former. This large surface-to-volume ratio can be an advantage for some applications, for example sensor devices [136-142]. However, it can also be a problem in other applications, for example, optoelectronic devices such as light emitting diodes [143] and solar-cell [144, 145] devices. Such surface states will strongly influence the electronic and optical properties at the semiconductor surfaces and interfaces since the surface recombination rate may become dominating, resulting in a short carrier life time [146-149]. The potential implications of these effects are especially noticeable in the case of nanostructure materials.
Now, I will give an concrete example to show how the surface recombination affect the carrier distribution in a p-type semiconductor subjected to illumination [130]. Assume that the illumination causes a uniform steady-state generation rate $G$. The continuity equation for electrons in one dimension can be described as:

$$\frac{\partial \Delta n(x,t)}{\partial t} = G - R + \frac{1}{e} \frac{\partial}{\partial x} J_n$$  \hspace{1cm} (2.1)

where $J_n$ is the current density caused by electrons flowing to the surface. In the bulk of a uniform semiconductor, there is no dependence on space and thus the continuity equation reduces to $G = R$ under steady-state conditions. Using the recombination rate in the bulk as given by Eq. (2.2),

$$\frac{d}{dt} \Delta n(t) = - \frac{\Delta n(t)}{\tau_n}$$  \hspace{1cm} (2.2)

the excess carrier concentration in the bulk is given by $\Delta n_\infty = G\tau_n$ as indicated in Fig. 2.10 (c). Assume that the electron current is diffusion current as described in Eq. (2.3).

$$J_n = eD_n \frac{\partial \Delta n(x,t)}{\partial x}$$  \hspace{1cm} (2.3)

Subsequently, we insert Eq. (2.3) into Eq.(2.1), the continuity equation for diffusive currents can be obtained

$$\frac{\partial \Delta n(x,t)}{\partial t} = G - \frac{\partial n(x,t)}{\tau_n} + D_n \frac{\partial^2 \Delta n(x,t)}{\partial x^2}$$  \hspace{1cm} (2.4)
As mentioned above, the carriers will rapidly recombine at the surface due to the existence of surface states in the semiconductors. So the boundary condition at the surface can be given by

\[ eD_n \frac{\partial \Delta n(x,t)}{\partial x} \bigg|_{x=0} = eS \Delta n(x,t) \bigg|_{x=0} \]  

(2.5)

where \( S \) is the surface recombination velocity. We assume that the generation rate is constant with time, thus the minority carrier concentration has no time dependence. The steady-state solution to the differential equation with the above boundary condition is given by

---

Figure 2.10: (a) Illuminated p-type semiconductor, (b) band diagram, and (c) minority and majority carrier concentrations near the surface assuming uniform carrier generation due to illumination. The excess carrier concentrations are \( \Delta n \) and \( \Delta p \).

[Reprinted with permission from Ref.[130], Copyright 2006 by Cambridge University press].
The carrier concentration near a semiconductor surface is shown in Figure 2.10 for different surface recombination velocities. For $S \rightarrow 0$, the minority carrier concentration at the surface is identical to the bulk value, i.e. $n(0) \rightarrow n_0 + \Delta n_\infty$. For $S \rightarrow \infty$, the minority carrier concentration at the surface approaches the equilibrium value, i.e. $n(0) \rightarrow n_0$.

\[
n(x) = n_0 + \Delta n(x) = n_0 + \Delta n_\infty \left[ 1 - \frac{\tau S \exp(-x/L_n)}{L_n + \tau S} \right] \tag{2.6}
\]

According to the surface recombination effect discussed above, it is worth to note that there is a very important parameter called “surface recombination velocity (in units of cm/sec)” that we should pay an extra attention, since it is usually used to specify the recombination at a surface[150]. On the basis of diffusion theory, the carriers in higher concentration regions are used to flow into the region with low carrier concentration. If the recombination rate is high in the region of surface, the minority carriers would be depleted. From this point of view, the moving rate of minority carriers to the surface will directly decide the surface recombination, which is called the "surface recombination
velocity". For instance, if the moving rate of minority carriers towards the surface is zero in a surface without recombination, the surface recombination velocity will be zero. On the contrary, if there is a infinitely fast recombination in a surface, the moving rate of minority carriers towards this surface is limited by the maximum velocity they can attain, and for most semiconductors in the order of $1 \times 10^7$ cm/sec.

The surface recombination velocities for several semiconductors are summarized in Table 2.3. The data shown in the table show that GaAs has a particularly high surface recombination velocity. One of efficient way to passivate the surface recombination is to reduce the number of dangling bonds. For thin films of semiconductor material, another layer is usually grown on top of them to tie up some of dangling bonds. For ZnO nanostructure, especially ZnO nanorods grown in chemical solution, the surface recombination has been passivated by both thermal post-annealing or increasing the growth pressure, which has been discussed in detailed in Paper III-VI.

2.4.4 Surface band bending

Since ZnO nanostructures usually have a very large surface-volume ratio, the band bending due to near surface on the PL process become more significant. Although as-synthesized ZnO nanostructures are usually n-type, both donor-and acceptor-like states are present within the band gap [151]. In this case, some donor electrons in the conduction band will reduce their energy by occupying the acceptor-like surface states. A negative surface charge is generated, counterbalanced by a positive space charge that originates from ionized donors within a depletion width $d$ away from the surface, such that overall charge neutrality is maintained. Consequently, a built-in electric filed and the corresponding electrostatic
potential will built up so that the energy bands bend upwards as they approach the surface and finally results in a surface depletion layer, which will strongly influence the PL properties of ZnO nanostructures [152-157]. The smaller a nanostructure is, the larger surface-volume ratio and stronger band bending effect it will have.

The width of the surface depletion region caused by adsorption can be described as [157, 158]

\[
d = \left[ \frac{2e_{\text{ZnO}}\varepsilon_0 \Phi_S}{e^2 N_D^+(T)} \right]^{1/2}
\]

where \( e_{\text{ZnO}} \) is the relative dielectric constant of ZnO, \( \varepsilon_0 \) is the permittivity of vacuum, \( \Phi_S \) is the height of potential barrier, \( e \) is the electronic charge, and \( N_D^+(T) \) is the temperature dependent activated donor concentration, which can be described as follows:

\[
N_D^+(T) = \frac{N_D}{1 + 2\exp\left(\frac{E_F - E_D}{K_B T}\right)}
\]

Using \( N_D^+(T) \sim 10^{17} \text{ cm}^{-3} \) at room temperature, \( e_{\text{ZnO}} \sim 8.7 \), and \( \Phi_S \) is of the order of 0.5 eV [156], the calculated width of depletion region is \( \sim 69 \text{ nm} \).

If \( D > 2d \), both the depletion region and non-depletion region can exist in the nanostructure, as shown in Figure 2.11 (a). If the nanostructure diameter \( D < 2d \), however, the nanostructure will be thoroughly depleted, as shown in Figure 2.11(b).

Under laser excitation, the photogenerated electrons and holes will be created. But they will be separated and swept in opposite directions by
Figure 2.11 Sketch of the energy band with different type of surface depletion region.
(a) partially depleted (b) thoroughly depleted.

the built-in electric field. For partially depleted case, as shown in Figure
2.11(a), the photogenerated electron-hole pairs created deeply within the
bulk have to diffuse through the bulk before reaching the surface
depletion region. Since the photogenerated minority holes have a shorter
diffusion length than the much more numerous majority electrons in bulk,
all of them will radiatively recombine with electrons before they can
reach the surface depletion region. Therefore, although the depletion
region exists in partially depleted case, as shown in Figure 2.11(a), the
chance of indirect recombination ($E_{ID}$) is quite smaller. So the direct
radiative recombination ($E_{D}$) in this case is the dominating recombination
channel. On the contrary, in the case of thoroughly depletion as shown in
Figure 2.11(b), since the nanostructure will be thoroughly depleted, the
photogenerated electrons and holes already in the surface depletion layer
can be effectively separated and accumulated at the edge of conduction
band and valence band without radiative recombination in the diffusion
process. Besides, if the energy difference between $E_{ID}$ and $E_{D}$ is smaller
(in our case only ~17 meV) than the thermal excitation energy of carriers
($KT\sim25$ meV) at room temperature, both indirect $E_{ID}$ and direct $E_{D}$
recombination will contribute to the UV emission process.
Chapter 3

Synthesis of ZnO Nanostructures

As mentioned in the first Chapter, ZnO is a versatile functional material. Except epilayer, it has a rich family of nanostructures such as nanotubes, nanowires, nanorods, nanobelts, nanorings, nanocages and nanosprings so on which can be fabricated by different techniques (see Figure 3.1[159]). In this work, we mainly investigated three types of ZnO structures, i.e. ZnO nanorods (ZNRs), ZnO nanotubes (ZNTs) and ZnMgO/ZnO heterostructures. In this chapter, I will introduce the detailed synthesis process of three samples one by one.

Figure 3.1: Different morphologies of ZnO nanostructures [Reprinted with permission from Ref.[159], Copyright 2004 by Elsevier Ltd.].
3.1 Synthesis of ZnO nanorods

As concerned as ZnO nanorods, although different fabrication methods, such as vapor-phase transport [22-24], pulsed laser deposition [25], chemical vapor deposition [26,27] and electrochemical deposition [6], have been widely used to prepare ZnO nanostructures, the complex processes, sophisticated equipment and high temperatures make them very hard to large-scale produce for commercial application. In recent years low-temperature wet chemical methods have received more and more attention and now already been commonly used to grow ZnO nanostructures. There are mainly three common approaches in chemical growth at low temperature, i.e. the hydrothermal [160-162], chemical bath deposition (CBD) [14, 28], and electrochemical deposition [163-165]. At here, we only choose CBD method to grow samples. One of its major advantages is that the growth temperature can be as low as 50°C. With such low temperature, much cheaper substrates such as plastic and glass can be used. And also there is a possibility to use p-type polymer as the p-type substrate when producing pn-junctions from ZnO nanorods, since the ZnO nanorods are n-type.

One problem is urgent to be solved for CBD method is that the nanorods grown on Si substrate show a poor reproducibility, difficulty to control size and bad orientation. Until now, the most successful approach for the CBD is growing ZnO nanorods on pretreated substrate, i.e. two-step CBD method [166-169]. Among those pretreated methods, thermal deposition [167], radio frequency magnetron-sputtering [168] and spin coating [169] techniques were usually applied to prepare ZnO seed layer on substrates. Clearly, the latter is much more easily carried out and the process is more economical. Therefore, we select spin coating technique
to introduce seeding layer on substrates and use CBD method to grow ZnO nanorods.

During the process of two-steps CBD, there are many parameters can be changed which will influence the structure and morphology of the sample. In this study, a few of them were investigated (see paper I). The parameters changed in this study are listed as follows:

- Seed layer
- pH value of chemical solution
- Angel $\theta$ between substrate and beaker bottom
- Growth time

After the systematical investigation, the optimized growth conditions to grow ZNAs were summarized out as follows: seed layer of ZnO nanoparticles, pH=6 and $\theta=70^\circ$. On the basis of it, we found an effective way to control the size of well-aligned ZNAs (see paper II).

In our experiments, all chemicals were analytical reagent grade and used without further purification. All the aqueous solutions were prepared using distilled water. Si (100) substrates were ultrasonically cleaned for 15min in ethanol before spin coating.

### 3.1.1 Substrate pre-treatment

Three different seed layers were chosen in our work, i.e. ZnO powder, Zn powder and ZnO nanoparticles. According to the seed layer of ZnO powder and Zn powder, the 0.005M suspension ethanol solution was prepared by ultrasonic technique and spin coated onto the solution for 4 times. The spin speed is 2000rpm and the spin time is 30s. And then the substrates were put into the oven for heating under 100°C for 10min in order to keep the seeds sticking onto substrates. For the seed layer of ZnO nanoparticles, zinc acetate dihydrate (Zn (C$_2$H$_3$O$_2$)$_2$·2H$_2$O) was
Figure 3.2: The low and high magnification SEM images of the sample grown on the Si substrate with different seed layer. (a)(b) bare Si; (c)(d)ZnO powder; (e)(f)Zn powder; (g)(h) ZnO nanoparticles.
dissolved in the pure ethanol with concentration of 5mM. This solution was coated for several times onto Si (100) substrates by a spin coater (Laurell WS-400-8TFW-Full) at the rate of 2000 rpm for 30s. The coated substrates were dried in room temperature and then annealed in air at 250°C for 30min. The annealed temperature of 250°C is a little above the decomposition temperature of zinc acetate particles in order to form ZnO nanoparticles seed layer. In the following, all substrates were pretreated twice for the above processes before final growth of ZnO nanorods.

Figure 3.2 shows the low and high magnification SEM images of the sample grown on the Si substrate with different seed layer. Compared with the sample bare Si, the seed layer of ZnO powder only makes the sample with higher density and the alignment is almost same. The seed layer of Zn powder makes the morphology of sample shows the flower shape. Only the sample grown on the Si substrate with the seed layer of ZnO nanoparticles has the best alignment and smallest diameter. The detail analysis of how the seed layer of ZnO nanoparticles affect the orientation can be found in paper I.

As a summary, the seed layer of ZnO nanoparticles is the most beneficial one for the growth of well-aligned ZNRs with small diameter. The study of other growth parameters changed can be found in paper I. The density of ZnO nanoparticles on the substrate can be controlled by the number of spin times, which can be used to control the size of ZNRs. The detailed processes and controllable mechanism have been described in paper II.

3.1.2 CBD growth

For CBD growth process, the aqueous solutions of zinc nitrate hexahydrate [Zn (NO₃)₂·6H₂O, 99.9% purity] and methenamine (C₆H₁₂N₄,
99.9% purity) were first prepared respectively and then were mixed together. The concentrations of both were fixed at 0.1M. The pretreated Si substrates were immersed into the aqueous solution and tilted against the wall of beaker. The angle between substrate and beaker bottom is \( \sim 70^\circ \). Then the beaker was put into the oven and kept in it for 2h at a constant temperature of 93°C. After growth, the substrate was removed from the solution, rinsed with deionized water and then dried at room temperature.

I also tried to change the growth pressure with sealing the beaker, the rest growth conditions are exactly same with above.

### 3.1.3 Annealing

For as-grown ZNRs, a post-growth thermal treatment was performed at 500°C, 600 °C and 700 °C respectively for 1h in air atmosphere and then quenched to room temperature by removal from the oven. This process is normally used to change the material properties.

### 3.1.4 Ammonia modification

Surface modification is an action of modifying the surface of a material, which provides an effective way to modulate the physical, chemical or biological characteristics different from the original ones, such as roughness, hydrophilicity, surface charge, surface energy, biocompatibility and reactivity.

To find an effective way to suppress the surface recombination, the as-grown ZNRs prepared in an open and sealed beaker were surface modified in 0.1 M (10ml) ammonia solution at 93°C for 15min. With
such short treating time, a devastating etching process does not happen on the surface, which has been testified by SEM results.

3.2 Synthesis of ZnO nanotubes

Among all one-dimensional ZnO nanostructures, the tubular structures of ZnO become particularly important since numerous applications, such as dye-sensitized photovoltaic cells [21] and bio/gas sensors[141, 142], are required their high porosity and large surface area to fulfill the demand for high efficiency and activity. Although the synthesis of ZNTs have been successfully realized by electrochemical method[7-9], low temperature solution method[5, 6, 10, 11], vapor phase growth[12] and so on. As a common knowledge, the reproducibility and control of growth in synthesis of ZnO nanostructures are a major issue. Among these methods, we prefer the simple chemical etching process to convert the ZNRs into ZNTs. One reason is that our technique to control the growth of ZNRs is already mature [170, 171], which can provide the precursor with appropriate size and good crystal quality for the conversion of ZNTs. The other reason is that previously we have not only already investigated the optical properties of ZNRs in detail, but also optimized their optical properties by effectively suppressing the surface recombination[172-175]. In this way, it is relative easier for us to reveal the luminescence mechanism of ZNTs through comparing the optical properties between ZNRs and ZNTs.

The ZNTs used in this investigation were synthesized by two-step process, i.e. growth of ZNRs and chemical etching process for converting ZNRs into ZNTs. Firstly, two ZNRs samples with the diameter of 120 and 280 nm were grown on Si substrates by the a two-step CBD method,
as mentioned in 3.1 section. The beaker was sealed during the growth process and the growth time was 3h. Subsequently, two ZNRs samples were respectively converted into ZNTs by chemical etching process. The chemical etching process was carried out by suspending the ZNRs sample upside down in 100 ml aqueous solution of potassium chloride (KCl) with 5M concentration for 10 h at 95 °C. In fact, the etching conditions can be optimized by varying the temperature, concentration of KCl solution as well as etching time to realize the transformation from ZNRs to ZNTs.

Now, I will discuss the conversion mechanism from ZNRs to ZNTs. Elias et al. pointed out that the selective etching to form hollow structures should be related with initial crystal structure of ZNRs due to no assistant reagents existed in the etching solution [9]. Two main factors will determine the conversion process from ZNRs to ZNTs. On one hand, the distinctive ZnO crystal habit exhibits a polar basal (0001) / top (0001) planes and six nonpolar (101 0) planes parallel to c-axis. The two polar planes are metastable due to the high surface energy, while the nonpolar (101 0) planes are the most stable ones due to the lower surface energy. So the Cl− ions might be preferentially adsorbed onto the top polar (0001) surface of the nanorods, which may result in the formation of a highly water-soluble zinc chloride complex such as ZnCl+, inducing the gradual dissolution of the nanorods core from the tip toward the bottom. As a whole effect, the etching rate is faster along polar plane than nonpolar planes. On the other hand, the defects in the ZNRs preferentially located near the crystal center, so that the preferential etching occurs from the center to form the tubular structures. It is well known that the smaller diameter of the nanorods, the more stable of the surface. Therefore, the ZNRs with smaller diameter are harder to be etched into tubular structures.
3.3 Synthesis of ZnMgO/ZnO heterostructures

To date, a number of research efforts have concentrated on the growth and study of ZnMgO epitaxial films, heterostructures, and quantum wells. Several techniques have been explored to successfully fabricate the ZnMgO epitaxial layers, such as molecular-beam epitaxy (MBE) [176-178], pulsed-laser deposition (PLD) [179-186] and magnetron sputtering[187-190], metal organic chemical vapor deposition (MOCVD)[191-194]. Among these techniques, the first three methods have disadvantages in mass production, due to high cost and low throughput. While, MOCVD has great advantages in terms of large-area deposition, atomic composition control feasibility and high deposition rate. Therefore, we utilized MOCVD to prepare ZnMgO ZnMgO/ZnO heterostructures in our work.

Figure 3.3: AIXTRON closed coupled showerhead (CCS) MOCVD system
An advanced AIXTRON closed coupled showerhead (CCS) MOCVD system was used to grown ZnO and Zn\textsubscript{0.94}Mg\textsubscript{0.06}O/ZnO heterostructures in our work. The pictures of system and chamber are illustrated in the Figure 3.3 and 3.4, respectively. For Zn\textsubscript{0.94}Mg\textsubscript{0.06}O/ZnO heterostructures, prior to any layer deposition, a sapphire substrate was annealed at 1100 °C for 5 min in a N\textsubscript{2} ambient. Then, a 306 nm ZnO buffer layer (named as ZnO-1) was deposited at 490 °C. In succession, a 440 nm ZnO (named as ZnO-2) was deposited at 950 °C. After that, the temperature was lowered down to 700 °C to deposit the Zn\textsubscript{0.94}Mg\textsubscript{0.06}O layer with 216 nm thickness. To compare with the annealing sample, a Zn\textsubscript{0.94}Mg\textsubscript{0.06}O/ZnO quantum well structure with five periods was deposited at 950 °C. The thickness of alternating Zn\textsubscript{0.94}Mg\textsubscript{0.06}O and ZnO layer is 10 nm and 3 nm, respectively. For the all layer deposition,
Diethyl Zinc (DEZn, (C₂H₅)₂Zn), bis-cyclopentadienyl Magnesium (CpMg) and N₂O (except ZnO-1 layer, tBuOH was used as O precursor) were used as the Zn, O and Mg precursors, respectively (except for the low temperature ZnO buffer layer, i.e. ZnO-1 in the structure, tBuOH was used as O precursor), which were carried with high-purity nitrogen gas at the flow rate of 9 liter/min. During the layer growth, the morphology evolution of the film surface was investigated by an in situ reflectance monitor system that comprises a modulated 635 nm laser diode beam.

After growth, the Zn₀.₉₄Mg₀.₀₆O/ZnO heterostructures were annealed in the tube furnace at 800 °C and 950 °C in N₂/O₂ (N₂ : O₂=2:3) mixed gas environment for 1h, respectively.
Chapter 4

Characterization Techniques

After the preparation of the samples, different characterization techniques were used to investigate their structure and optical properties. Scanning electron microscope (SEM) was used to get the morphology of the samples. An atomic force microscope (AFM) was utilized to detect the morphology of pretreated substrates and epitaxial layer. The detailed information about the structure of the samples can be obtained from transmission electron microscopy (TEM) and X-ray diffraction (XRD) measurements. The optical properties were investigated by micro-photoluminescence (PL), time resolved photoluminescence (TRPL) micro-Raman scattering, and resonant Raman scattering (RRS) measurements. X-ray photoelectron spectroscopy (XPS) was used to investigate the surface composition to identify the surface recombination centers. Secondary ion mass spectrometry (SIMS) was used to investigate the Mg diffusion behaviour in the ZnMgO epitaxial layers in detail. In this section, we will briefly introduce all these techniques.

4.1 Scanning electron microscope

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-
energy beam of electrons in a raster scan pattern [195]. The electrons interact with the atoms to make the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. The types of signals produced by an SEM include secondary electrons, back scattered electrons (BSE), characteristic x-rays, light (cathodoluminescence), specimen current and transmitted electrons. These types of signal all require specialized detectors for their detection that are not usually all present on a single machine.

Figure 4.1: Schematic image of SEM [196]
The schematic image of SEM is illustrated in Figure 3.3 in order to show how it works [196]. The SEM uses electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by heating of a metallic filament. The electron beam follows a vertical path through the column of the microscope. It makes its way through electromagnetic lenses which focus and direct the beam down towards the sample. Once it hits the sample, other electrons such as backscattered or secondary are ejected from the sample. Detectors collect the secondary or backscattered electrons, and convert them to a signal that is sent to a viewing screen similar to the one in an ordinary television, producing an image.

The SEM gives information on the surface morphology of the sample, which can help us check whether the growth has taken place or not. The SEM produces 2D images and reveals topographic features of the sample, which allows us to examine the diameter, length, shape and density of the ZnO nanostructures. However, the images from the SEM cannot definitively prove that the obtained nanostructures actually consist of ZnO. It can be obtained from energy Energy-dispersive X-ray spectroscopy (EDS), which is most commonly attached on the SEM system.

To characterize the morphologies of ZnO nanostructures and ZnMgO epitaxial layers, a JEOL JSM-6301F scanning electron microscope was used in our experiments. The chamber pressure is about 10^{-6} mbar. The gun voltage is 15kV. A max resolution of about 10nm can be achieved. Figure 4.1 illustrates the typical SEM images of as-grown ZNRs, ZNTs, ZnO and ZnMgO epitaxial layers.

According to Figure 4.2(a), the average diameter of ZNRs grown on the pretreated Si substrates for 2h is about 50nm. And the nanorods uniformly cover entire surface with high density and all the top surfaces
Figure 4.2: Typical SEM images from three type of ZnO structures. (a) top view of ZNRs; (b) cross sectional image of ZNRs observed from 45°; (c) top view of ZNRs which was used to convert into ZNTs; (d) top view of ZNTs; (e) top view of ZnO epitaxial layer; (f) top view of ZnMgO epitaxial layer.
of the nanorods were also hexagonal shape. Figure 4.1(b) illustrated the corresponding cross sectional SEM image. It indicates that the lengths of ZNRs are about 400 nm, which can be controlled by changing the duration of growth time. In Figure 4.2(c), we can observe the average diameter of ZNRs is ~280 nm. Figure 4.2(d) clearly shows that all the ZnO nanorods have been converted into nanotubes and the average wall thickness of the nanotubes is ~ 40nm. As shown in Figure 4.2 (e), we can see that the surface of ZnO epitaxial layer is flat and smooth. While, the surface of ZnMgO epitaxial layer as shown in Figure 4.2 (f) is not as smooth as that of ZnO epitaxial layer.

4.2 Atomic force microscope

To date, atomic force microscope (AFM) has become one of the powerful tools for imaging and measuring the nanoscale materials [197]. Binnig, Quate and Gerber invented the first AFM equipment in 1986, which is a type of scanning probe microscope with very high resolution in fractions of a nanometer, more than 1000 times better than the optical diffraction limit. The term 'microscope' in the name is a kind of imagery since it indeed gives the surface looking, while actually the information is gathered by "feeling" the surface with a mechanical probe.

Figure 4.3 illustrates the block diagram of AFM [197, 198]. The AFM consists of a microscale cantilever with a sharp tip (probe) at its end, which is used to scan the specimen surface. The cantilever is typically made of silicon or silicon nitride. During the measurement, a fine ceramic or semiconductor tip scans over a specimen surface in the same way as a phonograph needle scans a record. When the tip is brought into proximity of a sample surface, Van der Waals forces between the tip and the sample
lead to a deflection of the cantilever. The magnitude of the deflection is captured by a laser. A plot of the laser deflection versus tip position on the sample surface provides the resolution of the hills and valleys that constitute the topography of the surface. The AFM can work with the tip touching the sample (contact mode), or the tip tapping across the surface (tapping mode).

![Figure 4.3: Block Diagram of Atomic Force Microscope][1]

The AFM has several advantages over the SEM [197, 198]. (1) The SEM provides a two-dimensional image of a sample, while the AFM provides a true three-dimensional surface profile. (2) The samples viewed by SEM usually require metal/carbon coatings to improve the conductivity of the surfaces in order to enhance the resolution, which would irreversibly change or damage the sample. While, the samples can be directly measured by AFM without any preparation or pre-treatment. (3) An expensive vacuum environment is always needed for proper

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[1]: [Figure 4.3: Block Diagram of Atomic Force Microscope][1]
operation in SEM. While, most AFM modes can work perfectly well in ambient air or even a liquid environment, which makes it possible to study biological macromolecules and even living organisms. (4) AFM has been shown to give true atomic resolution in ultra-high vacuum, which means it can provide higher resolution than SEM.

Figure 4.4: The 1μm×1μm AFM image of the seed layer deposited on Si substrates for growing ZNRs.

Figure 4.5: The 1μm×1μm AFM image of ZnMgO epitaxial layer.
Figure 4.4 shows the 1μm×1μm AFM image of the seed layer deposited on Si substrates for growing ZNRs. From this image, it can be seen that the dispersion of ZnO nanoparticles is relatively uniform in the comparison with the nuclei formed on the bare substrates, and the average diameter and height of ZnO nanoparticles on the substrates is about 20nm and 3.5nm respectively. In the comparison between the SEM images of ZnO nanorods and the AFM images of pre-treated Si substrates, the relationship between the sample and seed layer is able to be revealed, which will be described in Paper II.

Figure 4.5 illustrates the 1μm×1μm three-dimensional AFM image of ZnMgO epitaxial layer. In light of the image, the film possessed hills and valleys morphology and the average roughness was calculated to be 20.35 nm.

4.3 X-ray diffraction

X-ray is a type of electromagnetic radiation with 1 Å (10⁻¹⁰ m) wavelength, appearing at the region between gamma-rays and ultraviolet, which is comparable with the size of an atom. The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at the atomic level [199].

When X-rays interact with a crystalline substance (phase), one gets a diffraction pattern [200]. To understand the basic principle of X-ray diffraction, we have to introduce the crystal lattice a little bit. In a crystal, the atoms do not distribute randomly but in a regular three-dimensional way in space, which comes into being crystal lattices. These lattices form a series of parallel planes with spacing distance d. Usually, the atoms distribute in a number of directions in any crystal, so that many planes
with different orientations exist and each of them has its own specific d-spacing. Figure 4.6 illustrates the reflection of x-rays from two planes of atoms in a crystal solid. When a monochromatic X-ray beam with wavelength \( \lambda \) is projected onto a crystal lattice at an angle \( \theta \), diffraction occurs only when the distance traveled by the rays reflected from successive planes differs by a complete number \( n \) of wavelengths, which leads to famous Bragg's Law:

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

(4.1)

where \( n \) is an integer 1,2,3,…., \( \lambda \) is wavelength in angstroms (1.54 Å for copper), \( d \) is interatomic spacing in angstroms, and \( \theta \) is the diffraction angle in degrees. By varying the angle \( \theta \), the Bragg's Law conditions are satisfied by different d-spacing in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the sample.

Based on the principle of X-ray diffraction, we can obtain a wealth of structural and physical information about the material. XRD has been
in use in two main areas: i.e. the fingerprint characterization of crystalline materials and the determination of their structure. On one hand, about 95% of all solid materials can be described as crystalline. Each crystalline solid has its unique characteristic X-ray diffraction pattern which may be used as a "fingerprint" for its identification. Today about 50,000 inorganic and 25,000 organic single components, crystalline phases, and diffraction patterns have been collected as standards. On the other hand, once the material has been identified, XRD may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the interatomic distance and angle are etc. From these points of view, we can see that X-ray diffraction has become a very important and powerful tool for the structural characterization in solid state chemistry and materials science.

Figure 4.7: Typical XRD pattern of ZnO nanorods.
Figure 4.7 shows the typical XRD pattern of ZNRs. All the peaks of the XRD patterns can be indexed to ZnO with the hexagonal wurtzite structure. In comparison with the standard card of bulk ZnO with hexagonal structure (see Figure 4.8), no diffraction peaks of other impurities are detected, which testify that the substance deposited on the substrates only belongs to ZnO.

4.4 Raman Spectroscopy

When a light come into a specimen, it will be scattered out. The light scattering process can be divided into two types, i.e. Rayleigh scattering and Raman scattering. For Rayleigh scattering, the incident photon is scattered elastically with unchanged frequency. For Raman scattering, the incident photon is inelastically scattered with a shift in frequency [203]. It is well known that the frequency shift of Raman
scattered light is related to the excitation frequency. However, it is worth to note that the magnitude of the shift is not dependent on the excitation frequency but the crystal structure. Therefore, this "Raman shift" can be attributed to an intrinsic property of the specimen. No doubt, Raman scattering is a powerful light scattering technique used to diagnose the internal structure of molecules and crystals [204].

Figure 4.9 Schematic images of Raman spectrometer [204]

Raman spectroscopy usually consists of three parts: Laser, spectrometer and charge-coupled device array (CCD) detector [204]. The spectrometer itself is a commercial "triple-grating" system. Physically, it can be separated into two stages, i.e. monochromator and spectrograph, which are shown schematically in Figure 4.9. Monochromater consists of two diffraction gratings (G1 and G2), bandpass slit between G1 and G2, and input/output focusing mirrors, which is mainly used as a filter. The incoming signal focused on G1 is separated into spread-out lights with different wavelengths travelling in different directions. These spread-out
lights then pass through the bandpass slit. We can adjust the slit width to only make the lights within user-defined range pass through and refocused on G2. The dispersion pattern in G2 is the mirror image of that from G1 so that the purpose of G2 is only to compensate for any wavelength-dependence in the dispersion of G1. After that, the light is finally refocused and sent out to the second stage of spectrograph which consists of another diffraction grating (G3) and two sets of lens. The filtered light from monochromater will be focused on the G3 and dispersed again. The dispersed light as a function of wavelength is recorded by a multichannel charge-coupled device array (CCD) in which different wavelengths can be read simultaneously. The obtained wavelength/intensity information is then input into a computer and converted by software into frequency/intensity. This is the raw data of Raman spectrum, which can be analyzed to obtain some information about structural properties.

Wurtzite ZnO belongs to $C_{6v}^4$ (P63mc) space group, with two formula units per primitive cell [205]. At the point of the Brillouin zone, group theory predicts the existence of the following phonon modes: $\Gamma = 2A_1 + 2B_1 + 2E_1 + 2E_2$. Among these modes, there are acoustic modes with $\Gamma_{aco} = A_1 + E_1$ and optical modes with $\Gamma_{opt} = A_1 + 2B_1 + E_1 + 2E_2$. The $B_1$ modes are silent modes. For the long-range electrostatic forces, both $A_1$ and $E_1$ modes are polar and are split into transverse (TO) and longitudinal optical (LO) phonons, all being Raman and infrared active. The $A_1$ phonon vibration is polarized parallel to the $C$-axis; the $E_1$ phonon is polarized perpendicular to the $C$-axis. The two $E_2$ modes ($E_2^{high}$, $E_2^{low}$) are nonpolar modes and are Raman active only. Every mode corresponds to a band in the Raman spectrum. Figure 3.11 illustrates the room temperature Raman spectrum of ZnO single crystal. All the modes of ZnO can be seen from this figure. The intensity of these bands depends on the scattering
cross section of these modes. For the polar modes, the scattering cross section of TO modes on only the deformation potential, but the LO modes depend, in addition, on the linear optoelectric effect. The linear optoelectric effect is attributed to polar phonon-induced macroscopic electric field coupled with excited electrons (Fröhlich interaction).

![Figure 4.10: Room temperature first-order Raman spectra of ZnO in scattering geometries corresponding to $A_1+E_2$ and $E_1$ symmetries [Reprinted with permission from Ref.[206], Copyright 2007 by the American Physical Society].]

The conventional micro-Raman spectra in our experiments have been collected in a confocal backscattering configuration under the 100x objective of an Olympus microscope. The 514.5nm line of a CW Ar-Kr-ion laser, Spectra Physics 2060, with a power of 5mW at the sample position, was used as probe. The cross-polarized scattered radiation was filtered by the first two stages of a triple grating Dilor XY 800 spectrometer, arranged in the subtractive configuration, to remove the strong elastic component, dispersed by the third stage, and recorded by a
liquid nitrogen cooled CCD camera, Wright Instruments. Figure 4.11 presents the typical Raman spectrum of as-grown ZnO nanorod arrays with 90nm diameter.

![Typical Raman spectrum of the as-grown ZnO nanorods array with 90nm diameter.](image)

To study the low-dimensional ZnO by Raman spectroscopy, the resonance condition is usually necessary due to two advantages as follows [207]. On one hand, the scattering cross sections of LO modes are larger than those of the TO, so in the Raman spectra the intensity of LO bands are remarkably higher than that of the TO bands. Therefore, LO bands are better candidates for investigating samples. However, the LO modes can be affected easily by other elementary excitation in the samples or external disturbances, and then their energy decreases. So, in the typical Raman spectra, the LO band has a low-energy tail. This broad line-shape will affect the discussion of the angular dispersion of LO phonon. To study the LO band, it is necessary to get rid of these
disturbances. Fröhlich interaction, which contributes to the scattering cross-section of LO phonon, is sensitive to resonance condition. Most of the disturbances are not sensitive to the resonance condition. In the resonance Raman spectra, only the LO modes and their overtones can be enhanced. So it can be assumed that in the resonance Raman spectra bands of LO and its overtones are pure super-positions of $A_1$-LO and $E_1$-LO modes.

Figure 4:12 Resonant Raman spectrum of as-grown ZnO nanorod arrays with 90nm diameter measured at the temperature of 175K.

In resonance Raman spectroscopy, the energy of the incoming laser is adjusted such that it or the scattered light coincides with an electronic transition of the molecule or crystal. For ZnO, a laser line with 351.1nm was used in our measurement. Figure 4.12 presents the resonant Raman spectrum of as-grown ZnO nanorod arrays with 90nm diameter. Four order of LO phonon lines can be seen from the sample.
4.5 Photoluminescence Spectroscopy

Photoluminescence (PL) is the spontaneous emission of light from a material under optical excitation [208]. PL measurement is a kind of powerful and nondestructive technique, which has been carried out on most of semiconductors. To date, there are many different type lasers have been widely used in the PL setup, for example, He-Cd laser with 325 nm, Ar⁺ laser with 316 nm/514 nm/488 nm, Nd:YAG pulsed laser with 266 nm, tunable solid state lasers and so on. When we use pump laser to provide pulsed excitation, the lifetime information of excited state can be obtained. Then the setup will be called Time-resolved PL (TRPL). When light of sufficient energy is illuminated a material, photons are absorbed and excitations are created. These excited carriers relax and emit a photon. Then PL spectrum can be collected and analyzed. However, only the energy of photons is equal to or higher than the bandgap, the absorption can happen in materials. Therefore, we have to choose different excitation source to do the measurements according to different material with different electronic band structure. The PL peak positions reveal transition energies and the PL intensity implicates the relative rates of radiative and non-radiative recombination. We also can change other external parameters during the PL measurement, such as temperature, excitation power and applied external perturbation such as magnetic field and/or electrical field and/or pressure, which can help us further understand the electronic states and bands.

Through PL measurement, we can obtain a variety of material parameters, which will be introduced respectively as follows[208]:

(1) Band gap determination

It is well known that the radiative transition between the bandgap in semiconductors is the most important one. So the PL measurement not
only helps us determine the bandgap of a semiconductor especially for a new compound semiconductor, but also guides us to accomplish the bandgap engineering, which is particularly significant for prompting the practical applications of a semiconductor in the industry.

(2) Impurity levels and defect detection

Usually, there are always some native defects and impurities in even pure semiconductors, which will form some localized defect levels between the bandgap. These defect levels certainly participate the radiative transitions. The PL energy associated with these levels can be used to identify specific defects, and the PL intensity can be used to provide a relative information concerning their concentration.

(3) Recombination mechanisms

It is well known that the "recombination" include both radiative and nonradiative processes due to the existence of the surface and defect levels in the bandgap. The PL intensity depends on the power of photo-excitation and temperature, which is determined by the dominant recombination process. Thus, analyzing power/temperature/time dependent PL spectra will definitely help us understand the underlying physics of the recombination mechanism.

(4) Material quality

The nonradiative recombination process in a material shows an obvious evidence for the existence of the defects. It is obvious that these defects are harmful for device performance. Through PL measurement, we can quantify the component proportion of nonradiative recombination in the emission process, which will help us judge the optical quality of the material is good or not.

The typical PL experimental set-up is illustrated in Figure 4.13. The samples were excited by a continuous-wave (cw) or pulse laser. The luminescence was resolved with a monochromator and detected by a high
Figure 4.13: Typical experimental set-up for PL measurements [208].

Sensitivity detectors depending on the detection range, for example, germanium detector for near infrared emission, CCD or a Hamamatsu R5509-72 InP/InGaAs nitrogen-cooled photomultiplier tube for UV, visible and near infrared emission[208].

In our measurement, the PL experiments were carried out in a variable temperature continuous-flow cryostat accessing the 1.5-300 K range. A CCD detector (Spectrum One) and monochromator HR460 from Jobin Yvon-Spex were used to disperse and detect the ZnO emission. Laser line with a wavelength of 266 nm from a diode laser (Coherent Verdi) pumped resonant frequency doubling unit (MBD 266) was used as excitation source.

The room temperature PL spectra of ZNRs and ZNTs are illustrated in Figure 4.14. Both samples show a dominant UV emission at ~382 nm and a very weak deep level emission (DLE) centered at ~520 nm. The origins of UV and DLE have been introduced in section 2.4.2.
Figure 4.14: Room temperature PL spectra of ZNRs and ZNTs.

Figure 4.15 illustrates the temperature dependent PL spectra from ZNRs and ZNTs. As observed in Figure 4.15 (a), the dominant peak at 3.362 eV is known as the donor bound exciton (D\textsuperscript{0}X) emission [209, 210]. The emission observed at 3.378 eV on the higher-energy shoulder of the D\textsuperscript{0}X peak is assigned to the free exciton (FX) emission [209, 210]. The variations of D\textsuperscript{0}X and FX peak position with the increase of measurement temperature are illustrated by the dot curves. It is obvious that the exciton emission shifts to lower energy and the FX become gradually stronger in intensity relative to the D\textsuperscript{0}X peak with increasing temperature. In addition, as temperature raises, the D\textsuperscript{0}X emission decrease rapidly than the FX emission due to thermal dissociation of the donor-bound excitons. Thus, the FX emission finally becomes prominent when the temperature is above 200 K. Grabowska et al pointed out that the quenching behavior of band-edge emission is very important in evaluating the effect of nonradiative centers in ZnO nanostructure materials [211, 212]. Under optical excitation, two competitive carrier quenching processes exist in
the materials, one is radiative and the other is nonradiative. Nonradiative recombination rates are generally thermally activated. If there is only one nonradiative recombination channel, one can obtain [211, 212]

$$I = I_0/[1 + a \exp(-E_a/kT)]$$

(4.2)

where $I$ is the PL intensities, $a$ is the process rate parameter, $k$ is the Boltzmann constant, and $E_a$ is the activation energy. According to the Eq. (4.2), the lower activation energy $E_a$, the more nonradiative contributions exist in a material. The detailed discussion about the evolution of PL intensity in ZNRs and ZNTs has been presented in Paper VII.

In addition, PL intensity is sensitive to radiative and nonradiative recombination lifetimes, $\tau_r$ and $\tau_{nr}$, respectively. We can utilize TRPL technique to get the lifetime information. TRPL was performed in our experiment by using an excitation laser line from a frequency tripled

Figure 4.15: Temperature dependent PL spectra for (a) ZNRs and (b) ZNTs.
sapphire: Ti laser emitting at 266 nm, a 0.3 m monochromator and a streak camera at 1.8 K. The TRPL spectra of ZNRs are illustrated in Figure 4.16. Generally, the PL decay rate of a semiconductor includes two components, i.e. radiative and non-radiative decay rates with a relationship of \( \tau_{PL}^{-1} = \tau_{NR}^{-1} + \tau_{R}^{-1} \), where \( \tau_{PL} \), \( \tau_{NR} \) and \( \tau_{R} \) are the time constants of PL, non-radiative and radiative decay, respectively[213,214]. We can obtain \( \tau_{NR} \) and \( \tau_{R} \) through fitting the decay curve by two exponential functions:

\[
I(t) = A_R e^{t/\tau_R} + A_{NR} e^{t/\tau_{NR}}
\]

where \( I(t) \) represents the PL intensity as a function of time, while \( A_R \) and \( A_{NR} \) are the relative weights of the two exponential decays with time constants \( \tau_R \) and \( \tau_{NR} \), respectively. After fitting work, we can reveal some detailed information about the nonradiative recombination. Thus, TRPL is a very powerful tool to analyze the nonradiative process.

Figure 4.16: Decay curves for 90 nm diameter ZNRs from as-grown sample and after annealing at 500°C for 1h. The decays were measured at 1.8 K. The color lines are the fitting curves according to Eq.(4.3).
4.6 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface analytical technique based on photo-ionization effect [215, 216]. In principle, when an X-ray beam illuminates the surface of a specimen, the core electron of an atom on the surface will absorb the entire X-ray photon energy. If the X-ray photon energy is higher enough, the core electron will then escape from the atom and emit out of the surface with certain kinetic energy, which is also called photoelectron. The kinetic energy $E_k$ of these photoelectrons can be determined by the X-ray photon energy $h\nu$ and the respective binding energies $E_b$:

$$E_k = h\nu - E_b$$

(4.4)

The experimentally measured energies of the photoelectrons can be given by:

$$E_k = h\nu - E_b - E_w$$

(4.5)

where $E_w$ is the work function of the spectrometer. Since we already known the X-ray photon energy and $E_w$, the kinetic energy is only determined by the binding energy. Every element owns more than one atomic orbital. The electron located at each atomic orbital has its unique binding energy like a “fingerprint”. With the X-ray excitation, each element will exhibit a set of peaks depended on the kinetic energies in the XPS spectrum. Usually, we plot the XPS spectrum as a function of binding energy instead of kinetic energy.

According to the work principle of XPS, we can identify almost all elements except for hydrogen and helium by measuring the binding energy of its core electron. Obviously, the presence of peaks at particular energies indicates the presence of a specific element in the sample. Furthermore, It is also worth to note that the chemical environment strongly influence the binding energy of core electron. With bonding to
different chemical species, the binding energy of a same atom varies, which leads to the shift of the corresponding XPS peak in the range of 0.1eV ~ 10eV. This effect is termed "chemical shift", which can be applied to studying the chemical status of element in the surface. In addition, the peak intensity in XPS spectrum is determined by the concentration of the corresponding element within the surface, thus XPS is also used to quantify the chemical composition.

![Figure 4.17: The picture of Scienta® ESCA 200 XPS equipment.](image)

In this work, XPS measurement was used to investigate the surface composition of as-grown ZNRs and ZNRs annealed in 500°C in order to identify the surface recombination centers. XPS measurements were performed on a Scienta® ESCA200 spectrometer (as shown in Figure 4.17) in ultra-high vacuum (UHV) with a base pressure of $10^{-10}$ mbar. The measurement chamber is equipped with a monochromatic Al (Kα) X-ray source providing photon with $h\nu=1486.6$ eV. The XPS experimental condition was set so that the full width at half maximum (FWHM) of the
clean Au 4f _{7/2} line was 0.65 eV. All spectra were measured at a photoelectron take-off angle of 0° (normal emission) and room temperature. The binding energies were obtained referenced to the Fermi level with an error of ±0.1 eV.

Figure 4.18 shows the XPS survey spectra from as-grown and annealed ZNAs, in which all of the peaks can be only ascribed to Zn, O, and C elements as labeled in Figure 4.18(b) [217]. It indicated that there were no other impurities observed in both samples. We would like to mention that, in all the XPS spectra of ZNAs, the binding energies have been calibrated by taking the carbon C1s peak (285.0 eV) as reference. The high-resolution XPS spectra of Zn and O elements and corresponding detailed discussion can be found in Paper V.

Figure 4.18: XPS survey spectra of as-grown ZNRs (a) and annealed ZNRs (b), where the labels indicated the origins of the corresponding peaks.
4.7 Secondary ion mass spectrometry

Secondary ion mass spectrometry (SIMS) is the most sensitive surface analysis technique to determine the elemental, isotopic, or molecular composition of the surface, which is widely used in materials science and surface science [218-220].

Figure 4.19: Typical schematic of a dynamical SIMS instrument [218].

Figure 4.19 illustrates the typical schematic of a dynamical SIMS instrument [218]. High energy ions are supplied by an ion gun (1 or 2) and focused on to the target sample (3). Usually, there are three basic types of ion guns [218]. The first type is the ions from gaseous elements, such as Ar⁺ or O⁺. Although the focus is rough, the current of ion beams is high. The second type is ion source from solid element surface, such as Cs⁺ primary ions, which can provide fine focus or high current depending on the gun design. The third type is liquid metal ion source, such as Ga and Au, which provides a tightly focused ion beam (<50 nm) with
moderate intensity and is additionally able to generate short pulsed ion beams. It is therefore commonly used in static SIMS devices. During the measurement, the ion gun will be chosen depending on the required current (pulsed or continuous), beam dimensions of the primary ion beam and on the target sample. When the surface of sample is bombarded by the high energy ions, some atoms will be ionized and sputtered out from the surface. These secondary ions are then collected by ion lenses (5) and filtered according to atomic mass (6), then projected onto an electron multiplier (7, top), Faraday cup (7, bottom), or CCD screen (8). The count rates of different secondary ion species give information about the composition of the sample in the sputtered area [219]. During a measurement, the sample is slowly sputtered (eroded) away and that is why SIMS is capable of measuring depth profiles and perform 3-D measurements.

Figure 4.20 SIMS depth profile of Mg, Zn, Al and O elements in ZnMgO epitaxial layer grown at 700 °C.
In this work, time-of-flight SIMS (TOF-SIMS IV instrument from IONTOF GmbH) was performed on Mg Zn$_{0.94}$Mg$_{0.06}$O/ZnO heterostructures to record the diffusion behaviors of Mg under different annealing temperature with 3 keV Ar$^+$ as a primary ion. The beam current was kept at 50 nA. The time of the analysis was converted to the respective depth assuming a constant sputtering rate. Figure 4.20 gives the SIMS depth profile of Mg, Zn, Al and O elements in Zn$_{0.94}$Mg$_{0.06}$O/ZnO heterostructure grown at 700 °C. We can observe that the Zn and O signals keep constant until reaching the sapphire substrate. On the contrary, Mg and Al signal decrease in the totally opposite directions, which clearly indicates that both of them diffuse into the ZnO-1 and ZnO-2 layers.

The diffusion processes of matter from regions of high concentration to that of low concentration are governed by Fick’s law. Actually, the Fick’s second law fit our situation very well, which can be described as[221, 222]:

\[
\frac{\partial^2 C(x,t)}{\partial x^2} = D \frac{\partial^2 C(x,t)}{\partial t^2} \quad (4.6)
\]

where \( C \) is the concentration of diffused impurity, \( D \) is the diffusion coefficient, \( x \) is the depth below the surface and \( t \) is the annealing time or growth time. For the thin film geometry, the solution of Eq.(4.6) is [222]

\[
C(x,t) = \frac{M}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \quad (4.7)
\]

where \( M \) is the total amount of source of diffusion. Eq. (4.6) is a Gaussian distribution function, which is easier to be fitted.

However, in our case, only one Gaussian distribution function is not enough to fit the curve. In principle, the diffusion coefficient in Zn$_{0.94}$Mg$_{0.06}$O layer and ZnO layers should be different. In addition, as discussed in XRD spectra, we already known that the lattice structures of
ZnO-1 and ZnO-2 layers are also different, which implies that the diffusion coefficients in them are different too. Therefore, we are trying to use three Gaussian distribution functions as followed to fit the experimental depth profiles:

$$C(x, t) = \sum_{n=1}^{3} \frac{M_n}{\sqrt{\pi D_n t}} \exp\left( -\frac{(x-x_n)^2}{4D_n t} \right)$$  \hspace{1cm} (4.8)

where $n$ (n=1, 2, 3) is integral number to distinguish three layers. We obtained the diffusion coefficient $D_n$ and revealed the Mg diffusion behavior under different annealing temperature. The detailed analysis can be found in Paper VIII.
In this thesis, the structural and optical properties of three types of ZnO structures, i.e. ZnO nanorods (ZNRs), ZnO nanotubes (ZNTs), and ZnMgO epitaxial layers, have been investigated in detail. The main results of each type of materials will be given as follows.

For ZNRs, we divided the investigation into two parts. One is focusing on optimizing growth conditions, realizing the size-controllable growth and revealing the controllable growth mechanism, which has been presented in Paper I and Paper II. The other is about surface recombination in the photoluminescence process, which has been involved in Paper III to Paper VI. All these results will be given by each of paper one by one.

Starting with Paper I, optimized growth conditions to fabricate well-aligned ZNRs on Si substrates have been obtained in two-step CBD method. The results show that substrate pretreatment, angel ($\theta$) between substrate and beaker bottom and growth time (t) indeed have great influence on the growth of ZNRs, and their influence mechanisms have been respectively explained in detail. The introduction of a ZnO nanoparticle layer on the substrate not only helps to decrease the diameter but also has a strong impact on the orientation of ZNRs. Under the growth condition of pH=6, $\theta=70^\circ$ and t=2h, the well-aligned ZnO nanorod arrays with 50 nm diameter was obtained on the pretreated Si
substrates. As-synthesized ZnO nanorods have a perfect crystallization and low density of deep level defects due to only a strong UV peak at 385 nm appears in room temperature PL spectrum for this sample.

In Paper II, on the basis of Paper I, the diameter of well-aligned ZNRs grown on Si substrates has been well controlled from 150 nm to 40 nm by two-step CBD. The effects of ZnO nanoparticles density and diameter on size and alignment of ZNRs were investigated in detail. In the comparison between the SEM images of ZnO nanorods and the AFM images of pre-treated Si substrates, the relationship between the sample and seed layer is able to be revealed. The results indicate that both diameter and density of ZnO nanoparticles will influence the size and alignment of ZNRs, but the density will play a key role to determine the diameter of ZNRs when the density is higher than the critical value of 2.3×10^8 cm^-2.

The results in Paper I and Paper II offer an effective way to solve the existing problems, such as reproducibility, size control and orientation of ZNRs, in CBD methods. Therefore, this study can not only provides a method for large-scale fabrication of ZnO nanorods with a low cost, but also open a way to the size-controlled fabrication of other materials by a hydrothermal approach.

In Paper III, the effects of annealing temperature on the structure and optical properties of ZNRs were investigated in detail. The results clearly indicated that the post-thermal treatment at 500°C in the air resulted in the CBD grown ZNRs with good crystal structure and good optical properties due to the decrease of surface defects. We also utilized Raman spectroscopy and low temperature PL measurements to identify, for the first time to the best of our knowledge, the surface defect contribution and outgoing resonant effect in RRS, which indicated that the Raman measurements can be used to monitor the change of surface
defects and deep level defects in the CBD grown ZNRs under thermal treatment from 500°C to 700°C.

In Paper IV, as discussed in Paper III, the surface defects indeed existed in the ZNRs, therefore, surface recombination may be play a great role in the optical properties of ZNRs. In order to testify it, the optical properties of the grown ZnO nanorods were investigated by a time-resolved photoluminescence spectroscopy. Three samples containing ZnO nanorods on Si (001) substrates with the diameter of 150, 90 and 60 nm, respectively, were used in this study. The results show that the effective decay time of the near bandgap recombination in the CBD grown ZnO nanorods strongly depends on the diameter of the ZnO nanorods. Typically, the decay curves obtained from these ZnO nanorods show a combination of two exponential decays. The experimental results show that the fast exponential decay is related to surface recombination and the slow decay is related to the “bulk” decay. The measured decay time of the effective surface recombination decreases with decreasing the diameter, while the “bulk” decay time remains unchanged. The results also show that an annealing treatment around 500°C significantly reduces the surface recombination rate. A simple carrier and exciton diffusion equation is also used to determine the surface recombination velocity, which results in a value between 1.5 and 4.5 nm/ps.

In Paper V, on the basis of Paper III and Paper IV, we utilized XPS technique to investigate the surface composition of as-grown and annealed ZNRs so that we can identify the surface recombination centers. XPS confirms the presence of OH bonds and specific chemisorbed oxygen on the surface of ZNAs, as well as H bonds on (10T0) surfaces which has been first time observed in the XPS spectra. The experimental results indicated that the OH and H bonds play the dominant role in facilitating surface recombination but specific chemisorbed oxygen also
likely affect the surface recombination. Annealing can largely remove
the OH and H bonds and transform the composition of the other
chemisorbed oxygen at the surface to more closely resemble that of high
temperature grown ZNAs, all of which suppresses surface recombination
according to time-resolved photoluminescence measurements.

In Paper VI, since we already identify the origins of surface
recombination in Paper V, it is relatively easy for us to find an effective
way to suppress the surface recombination during the growth process.
ZNRs are respectively prepared under different vapor pressure with
opening (OZN) or sealing the beaker (SZN). The results from time-
resolved photoluminescence measurements indicate that sealing the
beaker during the growth process can effectively suppress the surface
recombination of ZnO nanorods and the suppression effect is even better
than a 500°C post-thermal treatment to OZN. The results from X-ray
photoelectron spectroscopy measurement reveal that the main reason for
this phenomenon is that the surfaces of SZN are attached by groups
related to NH3 instead of the main surface recombination centers such as
OH and H groups in OZN. The ammonia surface treatment on both OZN
and SZN samples further testifies that the absorption of the groups related
to NH3 has no contribution to the surface recombination on the ZnO
nanorods.

The results from Paper III to Paper VI testify the existence of
surface recombination, reveal the important contribution of surface
recombination in the emission process, identify the surface recombination
centers and provide effective ways to suppress the surface recombination
during and after the growth process. All these results play an important
role to prompt the practical application of ZNPs in the fields of sensing
and photoelectronic devices.
For ZNTs, the structural and optical properties have been presented in Paper VII. ZNTs have been successfully evolved from ZNRs by a simple chemical etching process. Two peaks located at 382 nm and 384 nm in the UV emission region has been observed in the room temperature PL spectrum of ZNTs since the surface band bending in ZNTs induces the coexistence of indirect and direct transitions in their emission process. In addition, a strong enhancement of total luminescence intensity at room temperature in ZNTs has also be observed in comparison with that of ZNRs. Both temperature-dependent PL and TRPL results not only further testify the coexistence of spatially indirect and direct optical transitions due to the surface band bending, but also reveal that less nonradiative contribution to the emission process in ZNTs finally causes their stronger luminescence intensity. This work not only helps us well understand the optical mechanism of ZNTs, but also provides a promising nanostructural semiconductor candidate with good optical properties.

For ZnMgO/ZnO heterostructures, the structural properties, optical properties and annealing effects on the Mg diffusion behaviors in Zn\textsubscript{0.94}Mg\textsubscript{0.06}O/ZnO heterostructures have been investigated in detail. The Zn\textsubscript{0.94}Mg\textsubscript{0.06}O/ZnO heterostructures have been deposited on 2 inch sapphire wafer by metal organic chemical vapor deposition (MOCVD) equipment. Photoluminescence (PL) mapping demonstrates that Mg distribution in the entire wafer is quite uniform with average concentration of \textasciitilde 6%. The annealing effects on the Mg diffusion behaviors in Zn\textsubscript{0.94}Mg\textsubscript{0.06}O/ZnO heterostructures have been investigated by secondary ion mass spectrometry (SIMS) in detail. All the Mg SIMS depth profiles have been fitted by three Gaussian distribution functions. The Mg diffusion coefficient in the as-grown Zn\textsubscript{0.94}Mg\textsubscript{0.06}O layer deposited at 700 °C is two order lower than that of annealing samples, which clearly testifies that the deposited temperature of 700 °C is much
more beneficial to grow ZnMgO/ZnO heterostructures or quantum wells. This work optimizes the depositing conditions of ZnMgO/ZnO heterostructures or ZnMgO/ZnO quantum well structures, which plays a key role to prompt the practical applications of these structures.

In the future, this research will be extended into two directions. One is to fabricate ZnMgO/ZnO quantum well structures based on the results from the above Mg diffusion to optimize the growth condition for quantum well structures and to study their optical properties. The other is focusing on the applications of ZnO nanostructures, such as sensor, photoelectronic devices and so on.
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