Tailoring the electronic structures of zinc oxide based nanowires for optoelectronic applications

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**TAILORING THE ELECTRONIC STRUCTURES
OF ZINC OXIDE BASED NANOWIRES FOR
OPTOELECTRONIC APPLICATIONS**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

NANYANG TECHNOLOGICAL UNIVERSITY

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OPTOELECTRONIC APPLICATIONS**

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Abstract

ZnO nanowires (NWs) have attracted tremendous attention in the past 15 years after the first demonstration of optically pumped ultraviolet laser by Yang et al.^{1, 2} As a wide band gap (3.3 eV, RT) material possessing room-temperature stable excitons (60 meV binding energy), ZnO NWs have been treated as one of the most promising platform for next-generation optoelectronic devices.^{3, 4} The global lightening market calls for materials with controllable doping, energy band gap, as well as novel device design schemes to achieve high-efficiency devices emitting light with arbitrary mono or mixed colors.^{5, 6} In order to fulfill these requirements, we have synthesized ZnO NWs with designed electronic structures including 1) the *n-/p-type* doped MgZnO alloy wires where we tuned the carrier concentration and band gap simultaneously, 2) core/doped-shell NWs to spatially tuned band structure via integrated utilization of two growth methods: hydrothermal synthesis and pulsed laser deposition (PLD). The synthesized ZnO and ZnMgO NWs were characterized mainly by methodologies such as photoluminescence (PL) and X-ray photoelectron spectroscopy (XPS), etc. Self-consistent models were proposed to shine some light on the physical correlations between the carrier density, surface depletion, and luminescence, which could provide instructions on designing novel light emitting devices. Furthermore, taking into account conjugated factors aforementioned, we proposed a novel design scheme of ZnO NW-based white-light-emitting-diodes via Förster resonant energy transfer (FRET) from ZnO defect levels to quantum dots (QDs) and a prototype device was demonstrated for the first time.

The core part of the thesis could be divided into three main parts accordingly as follows:

Part-I Synthesis of MgZnO NWs with controlled conduction type via Ga and P doping

In Chapter 3, Ga and P-doped MgZnO nanostructures were synthesized by PLD to explore the possibility of modulating the band gap and conduction type simultaneously. The motivation of this work lay in the great importance of tuning the band offset ratio as well as extending the emission and transparent region of doped ZnO NWs. The Ga:MgZnO NWs array grew perpendicular to the sapphire substrates and the following XPS and PL confirmed the existence of gallium and magnesium. Under pulsed laser excitation, the doped wires exhibited Fabry-Perot lasing at 386 nm with a quality factor Q exceeding 1000.

For the P-doped MgZnO, the product displayed as very dense bundle of NWs with an hierarchical arrangement. The following XPS confirmed the successful incorporation of Mg and high concentration of P, which act as the key to compensate the background carriers and achieve *p-type*. Photoluminescence further confirmed the band gap tuning and existence of acceptor-related optical transitions. The stable *p-type* conductivity was proved by the fabricated homojunction *n*-ZnO thin film/P:ZnMgO NW diode, which shown rectification behavior even after three-month storage in air.

Part-II Forming ZnO/Ga:ZnO core-shell structure via doping gallium the surface to modulate the optical properties.

ZnO/Ga:ZnO core-shell NWs were fabricated to spatially tailor the electronic band gap via introducing the n^+ region near the NWs surface. This Ga-doped shells would act as the hole blocking layer preventing the non-radiative recombination of holes with trapped electrons induced by surface depletion effect. We have proposed an integrated electronic band structure model considering the conjugating factors such as mid-gap defects, surface depletion, and carrier concentration-induced band gap bending to explain the successful suppression of deep-level emissions (DLE). The following XPS measurement and temperature-dependent PL could fit the model very well. In short, this novel scheme and integrated model provided non-trivial physical insights on NW-based light emitting devices design and fabrication.

Part-III Excitonic energy recycling from ZnO defect states: towards electrically driven NW-QDs hybrid white light-emitting-diodes.

It is widely known that QDs, though be treated as eminent lumophores due to their high quantum yield and color tunability, are hinder in the path towards practical light emitting devices owing to the surface ligand-induced carrier injection difficulty. On another hand, as promising UV emitting material, ZnO NWs suffer from the undesirable visible emission due to the DLE, which result in uncontrollable emission color and waste of exciton energy. To address this problem, we proposed a novel device designing scheme for w-LEDs, which incorporated CdSe QDs with p -GaN/ n -ZnO NWs heterostructures. For the first time, QDs were excited by the recombination of carriers captured by deep-level states in electrically injected ZnO NWs. The device exhibited an achromatic emission with chromaticity coordinate (0.327, 0.330) and color temperature 5783 K, equal to the sun.

Chapter 1 Introduction

1.1 ZnO-base nanowires: The material perspective

The First decade of 21st century witnessed the rapid growth of solid state lighting market.⁷⁻¹¹ Contributing tremendously in this field “for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources” (quotes from the award ceremony speech), the Nobel prize was awarded to three researchers namely Nakamura, Akasaki and Amano who developed GaN-based light emitting diodes LED. As the rival of GaN, ZnO is also regarded as the promising building blocks for next-generation short-wavelength optoelectronics.¹²⁻¹⁵ Although ZnO was known to people as a direct wide band gap semiconductor in the 1960s, the surge in ZnO research occurred only after the first demonstration of nanowire laser in ultraviolet by P. Yang et al in 2001.¹

In the past 15 years of research, many amazing properties of ZnO were found or rediscovered. Compared to the nowadays industrial mature GaN, ZnO prevails in several aspects including¹³:

1) Large exciton binding energy

Excitons are quasi-particles consisting of an electron-hole pair bonded by coulomb interaction, which significantly enhances the wavefunction overlapping of them and promotes the radiative recombination.¹⁶ Possessing exciton binding energy as high as 60 meV is one of the most competitive traits of ZnO for optoelectronic applications. In contrast to 28 meV binding energy of GaN as well as most other semiconductors, excitons in ZnO could sustain at room temperature (corresponding to 26 meV thermal

dissociation energy), which makes it a competitive candidate for excitonic lasing devices.¹⁷

Figure 1.1 (a) 2014 Nobel Prize winners in physics for invention and development of GaN LEDs. (Copyright belongs to Nobelprize.org) (b) Photoluminescence Spectroscopy (PL) of the first nanowire-lasers in UV demonstrated by P.D. Yang. The inset was the scanning electron microscopy (SEM) image of ZnO nanowire array.¹

2) Availability of low-cost single crystal.

Owing to the nature of the triple bond between gallium and nitrogen, the growth of high-quality single-crystal GaN was once very challenging^{18, 19}. Until now, sophisticated high-temperature growth methods (most using metalorganic vapor deposition, known as MOCVD) are still indispensable in fabricating epitaxial GaN. However, large area, single crystal ZnO could be obtained economically via the traditional Bridgeman method, shown in Figure 1.2b.²⁰ According to G. Dhanaraj et al, the unit price in growing single crystal GaN is around 300 USD/cm², 50% higher than that of the ZnO single crystal wafer (data in the year 2010).²¹ Seemingly, the price

advantage for ZnO is limited. However, ZnO wafer production is not industrialized and there exists much space for further cost reduction, not to mention the possibility of growing single crystal via hydrothermal method, which is much less costly than aforementioned wafer production using high-temperature vapor method.

3) Resistivity to high-energy radiation.

Space-related applications require materials to show high-temperature tolerance, a high response rate as well as radiation robustness, especially for orbiters cruising in near-earth Van Allen belt which is flooded with energetic electrons and protons. D. C. Look proved that ZnO was more radiation-hard than common semiconductors and possessed potential in electronics working in extreme environments.²²

Physical parameter	ZnO	GaN
Molecular weight	81.389	83.729
Specific density, g/cm ³	5.642	6.11
Space group, lattice type	P6 ₃ mc (Wurtzite)	P6 ₃ mc (Wurtzite)
Lattice periods, Å	a=3.250, c=5.205	a=3.189, c=5.206
Melting point, K	2250	1700
Bandgap energy E _g , eV (RT)	3.37	3.39
Thermal coefficient of E _g , eV/K	-8·10 ⁻⁴	-6·10 ⁻⁴
Exciton binding energy, meV	60	21-28
Electron effective mass m [*] /m _e	0.24	0.2
Hall mobility of electrons, cm ² /V·s	120	900
Static dielectric constant	7.40 for E⊥c, 8.49 for E//c	12.2
Optical dielectric constant	for E⊥c, 3.72 for E//c	5.35

Table 1.1 Comparison of physical properties between GaN and ZnO.¹³

These outstanding characteristics render ZnO highly competitive in optoelectronics. In order to find the origin of these properties, people have researched deeply into the physical properties of ZnO such as the crystal structure, electronic band as well as optical transitions of this matter.

1.1.1 Crystal structure of ZnO

In nature, ZnO rarely crystallizes as single crystal and the synthetic is polycrystalline with white powder form. As a typical II-VI semiconductor, ZnO mostly crystallizes in three forms, namely rocksalt, zinc blende and wurtzite. While in ambient, wurtzite is the most thermodynamically preferable phase. The wurtzite structure manifests itself in a six-fold symmetric hexagonal unit cell belonging to the space group $P6_3mc$. There are two irreducible lattice parameters a and c , which exhibits $c/a = 1.633$ relationship in the ideal wurtzite lattice which is derived from the fact that wurtzite composed of two sets of hexagonal close-packed (hcp) atoms intersecting each other with $3/8$ displacement along c -axis. In this thesis, all the ZnO grown and characterized are all in wurtzite forms as shown in Figure 1.2c.

Figure 1.2 (a) Synthetic ZnO powder. (b) Wurtzite ZnO single crystal grown by Bridgeman method. (c-d) Ball-stick model of ZnO wurtzite structure, they are identical and the c -axis of (c) is the (111) direction of (d).²³

However, due to the ionic nature of the zinc-oxygen bond, the polar c-axis which is composed of alternating Zinc cations and oxygen ions would contract while non-polar a-axis would expand under the influence of Coulomb force. Thus the c/a ratio would deviate from the ideal value and fall within 1.5963 to 1.6035 depending on the specific preparation methods of the in-test samples. High-resolution X-ray diffraction (HRXRD) measurement results show that the lattice constant a and c vary from 3.2475 Å to 3.2501 Å and 5.2042 Å to 5.2075 Å respectively.²⁴

Figure 1.3 (a) calculated electronic band structure of wurtzite ZnO by SIC-PP method. (b) Comparison between calculated density and the experimental result.²⁵ (c) Fine band structure near the Γ point shows the threefold degeneracy at the valence band top.

1.1.2 Electronic band structure

The electronic band structure of a given semiconductor determines its potential application as optoelectronics.²⁶⁻²⁸ As aforementioned, ZnO is a semiconductor with a 3.4 eV direct band gap. The calculated²⁹ electronic band structure is shown as in Figure 1.3a together with the density of states (Figure 1.3b). The valence band top is a *p*-like state exhibiting threefold degeneracy due to the crystal field and spin-orbital interaction²⁴ shown in Figure 1.3c. The degeneracy would manifest itself in optical measurements with three distinguishable excitonic emissions and detailed discussion would be presented in the optical transition part.

For utilization in optoelectronics, it should be feasible to tune the band gap of the luminescent semiconductor in order to emit light in various wavelengths to cover the whole visible spectrum as well as forming energy barrier in quantum well structures.^{30, 31} Mg and Cd are the most maturely utilized two elements alloyed with ZnO to substitute cation forming solid solution for band gap engineering.³²⁻³⁵ Their lattice constants and band gap energy are shown in Figure 1.4.³⁶ To avoid metastable phase and phase segregation, there exists a upper limit in alloying concentration. The band gap of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ could be tuned up to 4.15 eV with $x \leq 0.36$ whereas the $\text{Cd}_y\text{Zn}_{1-y}\text{O}$ would be tuned down to 2.65 eV for $y \leq 0.53$.³⁷

Figure 1.4 Lattice parameter and band gap energy of II-O materials suitable for ZnO band gap tuning.³⁶

Another important aspect for optoelectronic application, especially for the wide-band-gap semiconductor, is the success of bipolar doping. ZnO is naturally *n-type* due to the unintentionally doped hydrogen or native lattice defect like Zn_i or V_O .³⁸ People have also successfully demonstrated *n-type* ZnO with high carrier concentration and resistivity as low as $1.2 \times 10^{-4} \Omega \text{ cm}$ for group-III dopants like Al and Ga.³⁷ The aluminum and gallium doped ZnO are competitive electrode candidates among transparent conductive oxides with whole visible range transparency and high conductivity.³⁹⁻⁴¹ The *p-type* doping, however, is very challenging to achieve. From the theoretical considerations, cation substitution with Group-I elements such as Li and Na as well as anion substitution with Group-V elements such as N, P, As are both able to form acceptor states^{39, 42-46}. Yet, series of experimental results shown that the most promising group-I element Li would occupy interstitial site and thus forming shallow donor states because of its small atomic radii.^{47, 48} The most thrilling results obtained in *p-type* doping for now is regarding N doping through repetitive modulation of growth

temperature reported by Kawasaki et al.⁴⁹ The low-temperature growth phase ensure that the N reside at the substitution site where as the high-temperature annealing phase kills the native point defects and minimize the self-compensating by those shallow donors. However, it is noticeable in their temperature dependent hole concentration measurement that the compensation ratio N_D/N_A ratio is higher than the samples grown in MBE methods and hole activation energy is around 100 meV, which implies an incomplete ionization of the acceptor.

Figure 1.5 The first demonstration of reproducible p-type doping methodology via repetitive temperature modulation in ZnO:N thin film growth. (a) Temperature ramping in the growth phase, indicating an alternative incorporation-activation procedure. (b) RHEED pattern shown that crystal quality would gradually diminish with the ongoing deposition at low-temperature while the short period of annealing could recover the crystalline revealed by the shrinkage of streak length. (c) Temperature dependent hole concentration plot with an inset of magnetic field dependent hall measurement.

1.1.3 Optical Property of ZnO

Strongly correlated to the electronic band structure and high exciton binding energy, optical transitions near band edge in ZnO are dominated by the free and bound exciton-related emission.⁵⁰⁻⁵⁵ As mentioned in the electronic band structure of the ZnO, the free exciton emissions originating from the conduction band to the three-fold degenerate valence bands are usually denoted by FX_A (heavy hole band), FX_B (light hole band) and FX_C (crystal field split band).^{56, 57} In samples with high crystal quality, photoluminescence measurement with high spectral resolution is able to resolve the two electron satellite (TES) and series of longitudinal phonon replicas of aforementioned excitonic emissions.⁵⁸ The TES transition behaves very similar to auger emission in the way that both transitions require two strong correlated dipoles. With the assist of the TES, people could calculate accurately the corresponding donor binding energy (E_D) based on the fact that the energy spacing between the donor bound exciton (D_0X) and its TES equals to three-quarters of E_D . It is worthwhile to mention that the origin of certain peak could not be reasonably justified solely on its energetic position unless researchers have enough supplementary characterization results to correlate with photoluminescence spectrum.

Figure 1.6 (a) Radiative recombination centers in the semiconductor.⁵⁹(b) Typical cathodoluminescence (CL) spectrum of undoped ZnO nanowires at 10 K. (DOI: 10.5772/39507)

Another prominent feature of ZnO PL is the strong deep-level-emission (DLE) in the visible region.⁶⁰⁻⁶³ Depending on the peak position and the line shape of the PL spectra, the emission bands are further categorized into green luminescence band (GL), yellow luminescence band (YL) and red luminescence band (RL). Amongst them, the

GL around 2.5 eV usually dominates the DLE and the origin of the emission is still controversial.⁶⁴ In most cases, the GL with distinctive fine peaks is related to copper doping whereas the broad featureless GL are most probably due to intrinsic defects. Usually, the yellow band emission around 2.2 eV is found in Li-doped samples. Yet, there are also a few reports on the YL in undoped samples. As for the RL around 1.75 eV, samples annealed in the air are likely to exhibit.³⁷

1.2 ZnO-based nanowires: The growth perspective

As have mentioned, the renaissance of ZnO accompany the research favor in the emerging semiconductor nanowire optoelectronics and photonics.^{65, 66} Originally, this trend is boosted by the increasing concerns regarding the high-frequency constraints of electronic devices and miniaturization limitation of Moore's law.^{27, 67} People endeavor to seek alternatives in devices which manipulate photons rather than electrons due to the native higher bandwidth and absence of joule heat⁶⁷⁻⁶⁹. As the first materials exhibiting lasing in hundreds of nanometer scale in size, the ZnO nanowire structure is treated as one of the most promising semiconductor cornerstones in realizing the next-generation miniaturized optoelectronic and photonic devices⁷⁰⁻⁷². With the development of nano-photonics research, more and more favorable traits of nanowires as well as "quantum" material have been integrated into the novel devices, such as the quantum-size effect, enhanced light-matter interaction, large surface to volume ratio, etc. However, advanced applications rely on the availability of high-quality materials. The traditional top-down lithography method has already encountered its limitations in defining feature smaller than 10s of nm, not to mention the deleterious effects coming from etching-induced surface defects.^{73, 74} Thus, more attention has been paid to

bottom-up routes, taking advantage of epitaxy, self-assembly, catalyst-assisted synthesis, and heterogeneous crystallization, to grow intrinsic or arbitrarily doped nanowires. In the following two sections, several chemical and physical bottom-up growth methodologies have been briefly reviewed.

1.2.1 Chemical vapor deposition

In the first demonstration of nanowire laser by P. Yang et al., the ZnO NW array was grown on sapphire substrates by gold-catalyst assisted carbothermal method in a typical chemical vapor deposition (CVD) set-up.¹ The growth follows the vapor-liquid-solid (VLS) mechanism where the Zn vapor and oxygen dissolve into the gold catalyst droplets and they react and crystallize at the droplet-solid (whether substrate or as-grown nanowire tips) boundaries. The substrates utilized in this method guarantee the NWs array to grow in excellent alignment with c-axis of ZnO perpendicular to the sapphire (110) surface, which is highly favorable for forming electrical contacts in optoelectronic applications. Though feasible to implement, VLS growth route highly relies on nanometer size metal droplet catalysts, resulting in unintentional doping and difficulties in fabricating controllable electrical contacts.^{25, 75} Thus, researchers tend to seek catalyst-free growth method and Hahn et al. realized the vapor-solid (VS) growth of ZnO nanowires on the quartz tube in CVD furnace as well as on Si substrate via direct oxidation of zinc powder for the first time.⁷⁶ They proposed that the evaporated zinc vapor would condensate at the substrate surface and aid the successive VS growth at the initial stage of the growth. Yet their growth model was lacking in the support from in-situ monitoring data thus the model remained a theoretical implication in the field of ZnO NWs. It is worthwhile to mention that nanowires grown in VS route usually exhibited higher randomness in growth orientation and reports on its successful applications in the epitaxial array are still rare.

Figure 1.7 Two growth mechanisms of CVD (a) VLS growth mode (b) VS growth mode⁷⁷

1.2.2 Hydrothermal

In contrast to the high temperature (higher than 800 °C) needed for the CVD growth, the low-temperature hydrothermal synthesis method is widely used in ZnO nanostructure synthesis and could also produce high-quality nanowire array⁷⁸⁻⁸². The schematic of the hydrothermal is shown in Figure 1.7, where the reactor is simply composed of a steel autoclave together with a PTFE vessel containing the precursors. Several pieces of substrates like sapphire or GaN would be mounted on a PTFE micro-rack with their epitaxy-ready surface facing down. Then the vessel would be loaded in the auto-clave and heated in an oven or on a hot-plate to initiate the synthesis.

Figure 1.8 (a) Steel auto-clave and its contain PTFE reactor in (b).

Vayssieres et al were among the first researchers who notice the possibility of applying hydrothermal in synthesizing nanowire array with control orientation.⁸³ Afterwards, their preference of combining zinc salt with hexamethylenetetramine (HMT) is widely accepted and the reaction mechanism is generalized in the equations below.

It is worthwhile to mention that the first two reactions are all reversible involving hydrolysis of the weak base HMT, which is of great importance for forming uniform and oriented nanowires. On one hand, Sugunan et al treated HMT as a non-polar surface capping agent able to induce *c*-axis preferential growth. On the other hand, most other researchers reckon HMT solution to be a kinetic buffer capable of gently releasing of OH^- by slow hydrolysis.⁸⁴

1.2.3 Pulsed laser deposition (PLD)

Besides the chemical methods reviewed above, PLD, (once called laser ablation) technique is also a widely utilized physical vapor deposition (PVD) technique for ZnO nanowire synthesis^{41, 85-88}. The system is composed of an excimer or Nd:YAG laser, vacuum & gas control, heating components, optical components as well as mechanical components. The mechanism of deposition is straightforward as shown in Figure 1.9 High power nanosecond laser is focused into a vacuum chamber and ablates the target made of sintered ZnO powder. The power density at target surface is able to reach 10^8 W/cm², heating material at the focus point to tens of thousands kelvin. The molten species evaporate and ionize by the laser EM field, forming the plasma plume. Then the plasma expands from the target to the substrate, where they cool down and condensate either as thin film or nanostructures. To understand thoroughly these procedures, PLD are mostly examined in three successive phases: 1) ablation phase 2) plasma plume phase 3) growth phase.⁸⁸⁻⁹¹

Figure 1.9 Schematic of pulsed laser deposition method. Besides the lens, all the other components are mounted inside a vacuum chamber, which is intentionally omitted for clarity of demonstration.

The unique advantage of the PLD is the ability to achieve congruent evaporation, which takes place at ablation phase^{92, 93}. In other vapor deposition methods of multi-compound material, the materials with lower boiling point would vaporize first when heat is applied. Yet, in the ablation phase of PLD, free electrons ejected from laser spot on the target were further accelerated by the light. Then they collide with atoms within the bulk target and transfer energy to ambient material within very short duration, typically several ps.⁹⁴ Thus, the heat generated in this process is confined to a very limited volume and the system can be regarded as quasi-adiabatic. The material is heated to 10^4 K. Thus, all species of different boiling points would evaporate simultaneously.⁹⁴

At the end of the ablation phase, a plasma plume composed of highly energetic ions, neutral atoms, electrons and particulates is generated, which consists the congruent composition of the target. Afterward, the plasma plume expands from the target to substrate. In this plume phase, several parameters such as laser spot size, pulse duration, background gas atmosphere, and chemical nature of the target would influence the energetic species as well as the shape of the plasma. Amongst these parameters, background gas is the key parameter in modulating plasma and thus controls the nanostructure morphology. The high-pressure (1-100 Torr) inert gas (Ar or N₂) with small portion of oxygen is commonly injected into the vacuum chamber to confine the plume into a small sphere, which acts as a homogeneous source of ZnO ions or small atomic clusters.⁹⁴⁻¹⁰⁰

When the energetic species reach the surface of the substrate, they would experience several competitive procedures including adsorption-desorption, nucleation-crystallization, “bonding with substrate”, and “bonding with nearby deposited species”. Herein, two factors play the roles of great importance: temperature and surface energy.

In crystallization process, the system tends to minimize its total surface energy. Thus, the island growth mode, which favors the growth of nanostructure, would dominate if the bonds between these deposited species are stronger than the bond with substrate. If not, monolayer growth mode preferred in the thin film growth would prevail vice versa.⁹³

In summary, these three methods are the most common growth routes to synthesize ZnO nanowires. The PLD method often yields materials with high optical and crystal quality. And the dopants could be easily incorporated due to the congruent evaporation. However, the ZnO nanowires obtained from hydrothermal methods usually exhibit strong defect-related emissions, indicating poor crystal and optical quality. Meanwhile, it is very hard introduce doping in the hydrothermal process due to the low growth temperature. The CVD methods are also feasible in growing high quality undoped ZnO nanowires. However, it is difficult to precisely control the doping concentration due to the different flow rates of the source materials with various boiling points.

1.3 ZnO nanowires: The surface depletion perspective

There exists a controversial physical phenomenon in the optical property of the ZnO nanowires^{26, 101-104}. As we have mentioned, each individual ZnO NW could be treated as one tiny single crystal, which is expected to show outstanding performance in optoelectronics. However, the preliminary research results reveal that photoluminescence (PL) of ZnO NWs highly depends on not only the growth method, chemical composition, annealing condition but also the diameter of the wires. This behavior is rather quizzical and Shalish et al originally owed this phenomenon to surface induced deep-level emission.¹⁰⁵ They argued that the surface of ZnO had much higher density of defects than the single crystal core part. Thus an as-grown ZnO nanowire was simplified as a core-shell wire, where the shell emitted light in the visible range (around 550 nm) and the central part illuminated in UV range. The model is shown in Figure 1.10.

Figure 1.10 (a) Scanning electron microscopy images and PL measurements of ZnO nanowires grown under the same condition but with different diameters. (b) Fitted dependence of NBE/DLE ratio on the nanowire radius.¹⁰⁶

Although this model fitted the experimental data well and intuitively followed previous knowledge regarding the surface to volume ratio effect, it could not be

overlooked that the DLE spectra line shape obviously changed with the diameter. We could defer that some significant information must be missing in this model.

As the optical property reflects the electronic structure of the material, Shalish's work provoked the curiosity towards the surface-induced modification of carrier behavior. Yu et al picked up what precedence ignored and studied the temperature-dependent PL of DLE. The results showed that the luminescence components had different dependence on temperature and they came up with a more comprehensive model which took into account surface depletion effect and correlated the surface with the core by a unified Fermi level¹⁰¹. The results provided a more accurate and reasonable description of the influence of surface on the optical property of nanomaterials.

Figure 1.11 (a) LTPL of DLE from ZnO nanowire. (b) A comprehensive model of surface depletion modified carrier recombination process. The band gap bends due to depletion of delocalized electron by the surface adsorbed oxygen. The surface state would also induce a lateral built in potential attracting holes to recombine nonradiatively with trapped electrons.¹⁰⁷

To mitigate this detrimental effect, series of methods have been proposed including the surface passivation by a dielectric material and surface modification through ion injection. But the surface layer would also introduce somewhat difficulty in carrier injection due to their much lower conductivity.¹⁰⁸⁻¹¹⁰

1.4 ZnO nanowires: The application perspective.

Due to the inherent single crystal quality of individual wire, ZnO NWs are very promising material platform to achieve high-efficiency electroluminescence^{50, 111, 112}. In the following parts, applications of ZnO nanowires in light-emitting diodes, and electrically pump lasing are reviewed with focus while another prototype optoelectronics are concisely introduced.

1.4.1. Light emitting diodes

Light emitting diodes are devices converting electrical energy towards photon energy via radiative recombination of electrons and holes, namely the electroluminescence (EL).¹¹³ According to the report from International Energy Agency, the lighting accounts for 20 % of global electricity consumption. Being more energy-efficient, LEDs are taking over growing market share from the traditional incandescent bulbs. The external quantum efficiency of the LED, defined to be the ratio between the amounts of emission photons/amount of injected electron-hole pairs, is determined by the parameters in the equation.

$$\text{EQE (External quantum efficiency)} = \eta_{\text{Inject}} \times \eta_{\text{IQE}} \times \eta_{\text{Extrac}}$$

Herein the η_{Inject} , η_{IQE} and η_{Extrac} denote the carrier injection efficiency, internal quantum efficiency and the light extraction efficiency, respectively. Due to the superb crystal quality, nanowires p - n junctions or quantum wells possess inherent higher internal quantum efficiency the commercial GaN thin film LEDs with the similar degree of quantum confinement.⁶⁶ The light extraction in the thin film LED is another problematic issue due to the large refractive index contrast-induced total internal reflection. Based on simple Snell's law calculation, the extraction efficiency could be improved by introducing a modified emission surface, either by shape modulation or

plasmonic effect.¹¹⁴ Nanowires, on the other hand, could be regarded as small waveguide fibers with end facets acting as scattering center. Thus, the ZnO nanowires array has also been widely grown on the thin film LED surface as a passive layer to aid the light extraction procedure.

To make the full use of the ZnO excitonic emission, an ideal structure of LED should be based on the MgZnO/ZnO/MgZnO or ZnO/CdZnO/ZnO core-shell quantum-well nanowires. Yet, due to the difficulty in achieving the stable *p-type* ZnO, people endeavor to integrate ZnO nanowires in alternative structures like *n-ZnO/p-GaN* as well.

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The first report regarding ZnO electroluminescence dated back to 1962, when Drapak et al found that ZnO single crystal exhibited EL around 520 nm. Shortly after that, they fabricated ZnO-Cu₂O heterojunction in the year of 1968. However, the EL is observed under both forward and reverse biases with spectra centering 540nm, the emission originated apparently from deep-level defect states.^{37, 66}

With the excitement of successful demonstration of ZnO nanowire laser, increasing efforts were devoted to developing electrically driven devices. The first ZnO vertical nanowire/whisker LED is demonstrated by Könenkamp et al in 2004 and the schematic of their device is shown in Figure 1.12¹¹⁷. The device could be simplified as a *p-i-n* diode where the nanowires acted as the intrinsic layer (though the wires were *n-type*, yet the SnO₂ and PEDOT:PSS had much higher carrier concentration). The EL turn-on voltage was around 10 V, much higher than the band gap ZnO, with the emission peak centering in visible region, even at the condition that the surface of the wires was passivated by the polystyrene.

Figure 1.12 (a) SEM images of as-grown ZnO nanowire. (b) LED device schematic (c) PL and EL of the fabricated device.¹¹⁷

The demand for the higher brightness requires the nanowire LEDs possess higher conductivity, which favors the *p-n* junction configuration rather than the aforementioned prototype. After Kawasaki et al.⁴⁹ demonstrated inspiring method of fabricating *p-type* thin film via repetitive thermal modulation in 2005, Chen et al.¹¹⁸ reported the near UV homojunction NW-LEDs using *in-situ* epitaxial growth of *P*-doped ZnO *p-type* nanowires on top of the *Zn*-doped ones. The electroluminescence spectra of the *p-n* junction wires centered at 342 nm as well as 480 nm, which coincides with the cathodoluminescence (CL) of the Zn:ZnO region in wires. Though they claimed they achieved the high-brightness NW-LEDs, the results are plausible in several aspects. First the rectification voltage of *p-n* junction initiated at 1 V, which were too small considering the 3.37 eV band gap of ZnO. Second, the LED ignited at 35 eV driven voltage and the emission peaks were very sparse and absent of continuous

peak shape changing with increasing forward voltage. Third, considering the mobility contrast of the electrons and holes, their claim that the emission happened in the *n*-type region might not be unquestionable.

Figure 1.13 (a) Device schematic and rectification behavior (b) I-V curve comparing the forward and reverse current (c) EL of ZnO homojunction LED under several biases.

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Considering the difficulties in achieve stable *p*-type ZnO with satisfactory electrical performance, *n*-ZnO/ *p*-GaN heterostructures have been proposed by Alivov et al^{119, 120} in 2003 as the alternative structure thanks to the breakthrough in the *p*-type GaN by Mg doping as well as the excellent lattice match between the ZnO and GaN (only 1.8% mismatch). However, the electroluminescence only showed a peak at 430nm, originating from Mg acceptor-related emission from GaN, indicating the existence of the unbalanced carrier injection due to the valence band offset and much higher mobility of electrons. Following his work, analogous structures in nanowires had been proposed and the initial works all suffered from high turn-on voltage and large

DLE/NBE ratio until Lupan et al demonstrated the electrodeposited ZnO nanowires on *p*-GaN shown in Figure 1.14, which exhibited high brightness emission in the UV/violate region and a 4.5 V EL emission threshold.¹²¹ Encourage by their work, researchers initiated to explore the possibility of realizing electrically pumped room-temperature laser.

Figure 1.14 (a) Band alignment of GaN/ZnO heterostructure (b) EL spectra of device under different bias.¹²¹

1.4.2. Nanowire laser

As another cornerstone for next-generation light-emitting devices, laser is an advantageous solution for applications where high output density, monochromatic, coherent light source is required. Rather than illuminate via the spontaneous emission, lasers rely on the stimulated emission in which light-matter interaction is enhanced by the existence of cavity. Lasers exhibit much faster on /off modulation and high power conversion efficiency, usually in the order of 50 %.⁵ Besides, nanowire has much higher light-matter coupling efficiency and could possess a larger than unity confinement factor according to Ng's report.¹²² Thus, beyond being efficient light emitting devices, miniaturized nanowire lasers play a significant role in communication and photonics circuits.

After the first demonstration of the photon-pumped laser based on ZnO NWs, J.L. Liu's et al.⁷¹ reported the first ZnO homojunction nanowire waveguide-laser pumped by direct current. The structure, which is grown by seed-assisted growth scheme, consists of Sb-doped *p-type* ZnO NWs/*n-type* ZnO thin film. The schematic of the laser diode device is shown in figure 1.15 and a low threshold current of 50 mA is achieved. The key to utilize the nanowire as the gain rather than thin film is to successfully obtain the *p-type* NWs, which could guarantee the radiative recombination happens most probably inside the wires considering the unbalance carrier injection efficiency. Their angular resolved far-field pattern characterized that the feedback is provided by Fabry-Perot cavity formed in such structure rather than random lasing.

Figure 1.15 (a) Schematic of electrically-driven ZnO nanowire homojunction laser diode. (b) EL spectra under 70 mA driven current and its side-view picture.⁷¹

D.Z. Shen et al.¹²³ reported another idea to design electrically pumped lasers fabricated from Au-MgO-ZnO metal-insulator-semiconductor heterostructures. The structure, I-V curve and EL spectra are shown in figure 1.16. The novelty of this structure lies in the use of large band gap insulating MgO thin layer as electron blocking layer aiding the carriers to accumulate and recombine at the MgO/ZnO interfaces where coherent random lasing forms. However, the turn-on voltage is higher due to the inefficient generation of holes through impact ionization process in MgO electron block layer.

Figure 1.16 (a) ZnO nanowire heterostructure laser with an inserted MgO thin film electron block layer. (b) EL spectra under different driven current ¹²³

1.4.3. Other applications in optoelectronics

ZnO photodetectors have long been a research field of interest due to their large photoconductive gain and transparency to visible light. Vapor-deposited ZnO nanowires clapped by Zn electrode were fabricated as photo detectors which exhibited very short response time (0.1ms rise time, deconvoluted exponential decay time 0.09ms and 0.36ms).¹²⁴ The sensitivity of ZnO to UV light originates from photoconductivity induced by its surface adsorbed oxygen and other gaseous species, as shown in Figure 1.17.¹²⁵ Thus the photocurrent highly relies on electronic property of the surface and the contact quality,⁶⁶ further resulting the response time of ZnO photo detectors ranging from nanosecond to several tens of second from case to case.³⁷

Figure 1.17 (a) Schematic of photodetectors based on photoconductivity of ZnO. After the light with higher energy than the band gap excites electron-hole pair nanowires the surface adsorb oxygen in (b) would be dissociated from the surface by the photo-generated holes and the remaining free electrons make the nanowire conductive, shown in (c).¹²⁵

As the representative work of the ZnO-NW-based ultrafast response, Soci et al demonstrated device with the fastest response to our knowledge.¹²⁵ They have applied 150-femtosecond laser to excite sample and recorded the rising time of the signal to be less than 1 ns. However, the recovery of the nanowire to the “off” state still required longer time (around 100 ns) and mechanism of this fast response was still not clear.

Different from Soci’s work, Yu et al fabricated the single ZnO NW/GaN thin film heterojunction as a photodetector. The photocurrent was induced by the separation of photo-generated carriers separated by space charge region rather than adsorption-desorption process. The prototype device displayed a rise time of 20 μ s and narrow wavelength response region (FWHM= 6.5 nm).¹²⁶

1.5 Objectives and significance of the study

Novel nanowire-based optoelectronics require ingenious design and control of electronic band structure to achieve satisfactory optical properties. Yet, in most cases, these two aspects of a certain nanowire could not be maximized simultaneously. Thus, the trade-off between the two conjugating factors necessitates deeper understanding of materials and increasing sophisticated methods to find the optimized design. This thesis endeavors to fulfill this aim using several methods as shown below to fine tailor the electrical band structure of ZnO NWs.

Part I: Synthesis of doped ZnMgO nanowires

To become the ideal material platform for optoelectronics require the broad coverage from UV to infrared range as well as higher conductivity. This work aims to explore the possibility of tuning the energy band gap and conductivity of the ZnO NWs simultaneously. The results showed the successful incorporation of dopants in the alloy nanowires. For the Ga:ZnMgO NWs, optically pumped lasing was achieved for the first time and the feedback mechanism was confirmed to be Fabry-Perot. And P:ZnMgO NWs exhibited stable p-type conductivity even after 3 months. Both the two types of wires exhibited blue-shift in the PL spectra, indicating the successful tuning of the energy band gap.

Part II: Ga:ZnO/ZnO core-shell nanowires

For the second part, we endeavor to enhance the optical property and electrical property simultaneously by designing a novel nanostructure, namely, the surfaced doped nanowires. By this design, carriers are confirmed to be confined in the undoped ZnO core which possesses higher crystal and optical quality. Through the LTPL, we confirmed the existence of the carrier confinement and proposed a comprehensive

model which correlated the carrier concentration, mid-gap defect states and surface depletion together aiming to provide an insight on high-performance nano-optoelectronic device design.

Part III: ZnO NW-CdSe QD hybrid LEDs

Energy injection for QDs could be another potential application for ZnO NWs. For the first time, we proposed to take advantage of the DLE states to facilitate the energy injection into the QDs as well as competitively consume the carriers which reside in those states with lower radiative recombination rate. By combining the EL of GaN, ZnO, and the CdSe QDs, we successfully demonstrated the white light-emitting-diodes with color temperature equal to the sun.

In summary, the internal correlations between my three works lie in the material platform used, i.e. ZnO nanowires. I studied the underlying physics of correlated factors, namely, surface, optical properties and electronic band structure of the ZnO nanowires to obtain insights into nanomaterial synthesis and optoelectronics applications.

Chapter 2. Experimental Techniques

2.1 Growth technique

In the Introduction part, we have already addressed briefly on the working principles of the growth methods utilized in the thesis namely the PLD and hydrothermal synthesis. In this part we would concisely introduce our experimental set-up.

2.1.1 PLD

The PLD system consists of a Compex Pro 205 KrF excimer laser, produced by Coherent. Co. The laser wavelength is 248 nm, possessing a maximum output power reaching 700 mJ per pulse with the pulse width equals to 25 ns. The laser spot has a size of 12 mm*25 mm and pass through two mirrors and an UV focusing lens ($f=1$ m). Then the focused beam shines on the ZnO-based targets in the LMBE 450 (Sky Technology, China). The base vacuum of our system could be pumped down to 10^{-6} Torr by turbomolecular pump. Gas flow of Ar, O₂, N₂ solely or their mixture could be injected with a control rate monitored by mass flow controller (MFC) to change the background atmosphere. The substrates are mounted on the heater which could reach as high as 800 °C and temperature is monitored by thermal coupler. After growth, samples all follow a cooling procedure with 10 °C ramping rate to 500 °C before the heater is shut down.

The c-sapphire substrates are used to grow the ZnO-based nanowires in this thesis due to its excellent lattice match with ZnO. They are cut into 1*1 cm² slices and washed in ultrasonic in acetone, isopropanol, and deionized water for 20 min, successively. Then the slices are blown dry by purified N₂ before loaded into the LMBE 450 chamber.

Figure 2.1 (a) KrF excimer laser for PLD. (b) LMBE-450 system

2.1.2 Hydrothermal

The Mg-doped GaN@Al₂O₃ substrates are used as growth template in hydrothermal method for the consideration of lattice match and fabrication of devices. The substrates follow the same washing procedure before loaded on the Teflon rack with GaN facing down. Then the reactor is put in the oven preheated to 95 °C. After reaction, the reactor would be put in atmosphere to cool down naturally to release the pressure. Then the samples are rinsed with DI water for three times to wash away the surplus precursor.

Figure 2.2 (a) Hydrothermal reactor and the rack in right part supports sample during the reaction. (b) Convection oven for hydrothermal reaction

2.2 Characterization technique

2.2.1 Scanning Electron Microscopy

Scanning electron microscope (SEM) is one of the most widely used sample morphology characterization methods. Imaging is realized by scanning the surface of sample with focus electron beam and analyzing the information contained in various kinds of signals, including secondary electrons, backscattered electrons, photons (cathodoluminescence), X-rays, etc. Amongst them, secondary electron signal is highly morphology sensitive and could resolve better than 1nm. In this thesis, all the SEM figures are measured by JEOL-6700F field effect scanning electron microscope (FESEM). Normally, the samples in-test should be fairly conductive to prevent the accumulation of electrons. Yet, due to the natural *n-type* of undoped ZnO nanowires, we did not coat any conductive layer at surface if without further notification.

2.2.2 Transmission Electron Microscopy

Imaging in TEM is produced by the absorption of the highly energetic electron beams by the sample¹²⁷. According to the De Broglie equation, the wavelength of any matter could be correlated to its kinetic energy by equations below.

$$E = h\nu; P = h/\lambda$$

For a field accelerated electron in the TEM, its E (energy) and P (momentum) could be calculated by the equation below

$$E = eV = \frac{1}{2} mV^2; P = mV$$

The results could be more precise after refined by the theory of relativity.

$$\lambda (\text{\AA}) = \frac{12.26}{\sqrt{V(1 + 0.979 \times 10^{-6}V)}}$$

Herein, the unit of V (voltage) is volt. At high resolution working mode, electrons are accelerated by 200 KV filed and the corresponding wavelength is around 0.0251 Å. Under that case, the electrons are more wave-like rather than particle-like. So the modulation of the image is due to the complex wave-interaction between the electron beam and material, not simple by absorption. TEM is usually equipped with energy dispersive X-ray spectroscopy (EDX or EDS), which can map the composition distribution of the sample. In this thesis, all the TEM images are taken using the JEOL 2100F with UHR Configuration as shown in Figure 2.3

Figure 2.3 JEOL 2100F TEM with UHR Configuration.

It is worth to mention that the selective area electron diffraction (SAED) is a powerful tool to resolve the crystal type and crystal quality of local region by electron diffraction pattern. In fact, the SAED could be viewed as a magnified reciprocal lattice of the specimen and the lattice parameters could be drawn out directly by measure the

spacing between the bright spots. The mechanism of the SAED is shown in the following figure¹²⁸.

Figure 2.4 Working mechanism of SAED. The circle of the blue dash line has a radius equals to the wave vector electron beam with purple arrow indicating incident beam. Any wave vector differentiates with the incident beam vector by a reciprocal vector would be able to produce a diffracted bright spot on the screen.

2.2.3 X-ray diffraction (XRD)

XRD crystallography is a powerful tool in material research which can give information of the crystal lattice by analyzing the angle and intensity of the diffracted X-ray. The working principle of XRD is similar with the SAED but the refracted beam intensity could provide composition information qualitatively due to reduced complex interaction between the less energetic beam and specimen than SAED. Usually, the samples are scanned in $\theta - 2\theta$ mode and the refracted peaks only reflect the lattice plane parallel to the sample stage. XRD patterns appear in the thesis were measured by the Bruker D8 powder XRD with a Copper radiation source ($1.54 \text{ \AA}$).

Figure 2.5 Bruker D8 Advance Powder X-ray diffraction

2.2.4 X-ray Photoelectron Spectroscopy (XPS)

XPS technique originates from the photoelectric effect and it is a surface-sensitive technology (less than 10 nm penetration depth) providing the composition information of the specimen^{129, 130}. The working principle of the XPS is shown in the figure below where an incident beam interacts with the core electron and excites them out of the sample. Then these ejected electrons are collected by the energy analyzer. The whole procedure follows the energy conservation law and could be expressed by the equation. Herein, the E_b , electron binding energy is the characteristic quantity we should extract. The $h\nu$ is the known photon energy of the X-ray incident beam (For Al source, photon energy=1486.6 eV). ϕ is work function of the detector (in 4-5 eV range) and E_k is the kinetic energy to be measured from the analyzer. Later on, ϕ could be eliminated by proper mathematical treatment.

$$h\nu = E_b + E_k + \phi$$

Figure 2.6 (a) Working principle of the XPS (b) Photoelectric effect in the generation of photoelectrons in XPS.

Herein, the composition and chemical states of ZnO-based nanostructures are measured by X-ray photoelectron spectroscopy (XPS) produced by Kratos AXIS Ultra. The monochromatic Al Ka X-ray radiation (15 kV/10 mA) served as the excitation source. The high-resolution spectrum studies of elements were conducted with an energy accuracy of 0.1 eV under 40 eV constant pass energy. To eliminate the ϕ induced spectra shift, all the data were calibrated by adsorbed carbon contamination peak at 284.8 eV.

2.2.5 Steady-state photoluminescence (PL) measurement

PL is a phenomenon where the specimen emits light due to the irradiation of excitation light⁵⁹. Herein, the steady-state means the excitation light source are continuous wave laser (cw-laser) or low power lamp, where there excitation would not significantly change the distribution of the carriers in the sample. In semiconductor, the excitation light generates electron-hole pairs bonded together by the lattice-screened

Coulomb interaction, namely excitons. Part of them recombines radiatively and forming the free exciton transition (denoted as FX). Yet, some others could be captured by impurities within the material and form a series of transition such as donor bound exciton (DX), acceptor bound exciton (AX), two electron satellite (TES). Moreover, the aforementioned transitions could also interact with the optical phonons and form series of replica transitions, equally spaced from their zero-order transition by quanta of optical-phonon energy. By carefully collect all these transitions signals and disperse them with fine gratings, information of the existence and ionization energy of the samples could be extract from the spectra non-destructively.

As for the photoluminescence of the semiconductor, the spectra shape would gradually broaden with the increasing temperature due to several broadening mechanisms and the quenching center would be also activated, both resulting in the blurring of the sample information. More importantly, for most of the semiconductors, the exciton binding energy and its impurity binding energy all falls in the 10-20 meV range (E_{Xb} , GaN=28 meV), making them easily dissociated by the increasing thermal energy. Thus, Low-temperature photoluminescence (LTPL), where the samples are loaded into a helium or nitrogen cooled cryostat, is introduced to measure the “fine structure” of the spectra.

Moreover, to spatially resolve PL from sample, micro-PL is also utilized to observe the sample emission through a microscope with tunable magnifications.

All the steady-state PL and LTPL spectra are measured using the experimental set up given in the schematic Figure 2.7. The 325 nm UV line from the He-Cd laser (IK series, KIMMON) were chopped by the mechanical chopper and passed through two Al mirrors before it reached the sample. Then the fluorescence from the sample (sticks

to the sample stage in the cryostat, 4K close-cycle helium, Advanced Research System Inc.) was collected and focused into the monochromator (Spectro 2750, Acton), where it was dispersed by metallic grating (600/mm). Then the detector, CCD/PMT, was used to collect the intensity signal and output the data to computer. When the PMT was activated, the signal is pre-processed by lock-in amplifier, which significantly increased the signal to noise ratio.

Figure 2.7 Schematic of the photoluminescence set-up

2.2.6 Transient PL measurement

Transient PL measurement could reflect the carrier recombination kinetics of a given material, which further facilitates the analysis about the microscopic origin of a luminescence center. Different recombination centers possess fluorescence lifetime ranging from nanosecond to tens of seconds. Therefore, specialized techniques are developed to measure the transient process in various time ranges. In this thesis, the band-edge emission and defect related emission of semiconductors are recorded by DCS-120 Confocal FLIM Scanning Systems (100 ps temporal resolution) and direct signal imaging in Tektronix DPO 7524 oscilloscope, respectively.

Figure 2.8 (a) DCS-120 Confocal FLIM (fluorescence lifetime imaging microscopy) system (b) working principle of TCSPC.

These two systems follow different mechanism of extracting transient data. The FLIM system is equipped with 375 nm laser and time-correlated single photon counting detector (TCSPC). In this term, “time-correlated” refers that the trigger of the excitation pulse correlates with emitted single photon induced voltage pulse. This

procedure is produced many times for the reason that the correct lifetime could be drawn out only under the condition where no more than one photon (could be zero!) is collected in each recording¹³¹.

By integrating data from multiple recording, a histogram could be plotted reflecting the recombination process of the specimen. Usually, the TCSPC is chosen when the lifetime falls within microsecond to hundreds of picoseconds.

On another hand, the direct imaging of the luminescence response was realized using a home-built set-up connecting the Hamamatsu R928 photomultiplier tube (PMT) in the monochromator to the oscilloscope (with rise time less than 2 ns). A tunable nanosecond laser is used (with a 6-9 ns pulse width, 20 Hz repetition rate) to excite the sample and the data are averaged over 500 cycles to increase the signal to noise ratio.

Chapter 3. Synthesis of MgZnO NWs with controlled conduction type via Ga and P doping

3.1 Introduction

MgZnO alloying is a powerful method to tune the electronic band gap to higher energy¹³². The extended band gap energy (E_g) would play a significant role both in expanding the transparency range of transparent conductive oxide (TCO) thin film as well as in deep UV optoelectronics. At 300 K, the E_g could reach as high as 3.8 eV for $Zn_{0.7}Mg_{0.3}O$ ^{2, 133, 134}

Though feasible in tuning the band gap energy, the Mg incorporation would deteriorate the conductivity of the alloy, thus undermining its potential applications in optoelectronic devices. In this chapter, doped MgZnO alloy nanowires would be synthesized with optical and electrical properties characterized by the photoluminescence and I-V measurement.

To achieve *n-type* doping, gallium was chosen as the dopant due to their comparable ionic radii with zinc which would introduce less lattice distortion, thus retaining the excellent optical property of ZnO^{4, 87, 135, 136}. As have been mentioned by Ma et al, Ga has higher resistance to oxidization and comparable donor ionization energy with Al^{137, 138}. Moreover, several groups have explored the possibility of applying Ga:ZnO in realizing semiconductor based plasmonics to mitigate the ohmic loss in the analogous metallic structures¹³⁹. Thus, Ga is an ideal dopant for achieving highly conductive MgZnO alloy.

To provide a potential route to solve the *p-type* problem in the ZnO, MgZnO alloy based *p-type* materials attracted much attention due to the ability to introduce extra V_{Zn}

by Mg incorporation^{2, 133, 140}. The V_{Zn} acted as *p-type* defect in the lattice and could supply high concentration of acceptor together with *p-type* dopant like phosphorus, which is of the key significance for compensating the excess donors in ZnO. Compared to other *p-type* dopants, P-doped ZnO shows elevated carrier concentrations and medium carrier mobilities. Thus, it is viewed as an important acceptor dopants to obtain high-quality *p-type* ZnO.¹⁴¹

Also, the ability to tune the band gap by incorporating the Mg would be feasible in spatially manipulating the carrier recombination and mitigating the inefficient interfacial recombination usually seen in the ZnO/GaN heterojunction. In this chapter, we would demonstrate the synthesis strategy of P:ZnMgO nanostructures. Together with Ga:ZnMgO nanowires, we would conduct a comparative research on both *n-* and *p-type* alloy nanowires, which provided clues about the physical origins of certain peculiar properties.

3.2 Experimental Process

3.2.1 Materials and Methods

Materials: ZnO target (99.999%, MOS group), MgO: ZnO target (10 at% Mg, 90 at% Zn), Ga₂O₃: MgO: ZnO target (5 wt% Ga₂O₃ 5 wt% MgO, 90 wt% ZnO), Acetone, 2-propanol, deionized water.

Growth equipment: LMBE-450 equipped with CompexPro KrF Excimer laser,

Characterization equipment: Bruker D8 advance XRD, Joel-6700F FESEM, XPS, PL and micro-PL.

3.2.2 Growth procedure

The Ga:ZnMgO nanowires followed the similar growth route with undoped ZnO nanowires. Prior to the anisotropic growth of NW, thin film of polycrystalline ZnO or Ga:ZnMgO buffer layer (for ZnO or Ga:ZnMgO sample, respectively) was deposited at 650 °C in 3.5 Pa O₂ atmosphere on the c-sapphire acting. Then temperature is increased to 800 °C in 15 min with the atmosphere adjusted to 1100 Pa (for ZnO) or 1076 Pa (for Ga:ZnMgO) Ar mixed with 10 Pa O₂. Then both the targets were ablated with 380 mJ laser pulses to growth the nanowires. After the growth phase, both samples were annealed in the identical atmosphere as in the growing phase following the annealing procedure shown in Chapter 2.

The P:ZnMgO NWs were grown on the undoped ZnO thin film for lattice match reason as well as for forming the *p-n* junction. Prior to the NW growth, the ZnO thin film was grown in 1×10^{-3} Pa O₂ at 700 °C using 260 mJ ablation laser with 5 Hz repetition rate. The total growth duration was 5000 pulses. Then the NWs were grown

in several O₂-Ar mixtures to optimize the growth condition. After growth, the NWs were annealed following the procedure in Chapter 2.

3.3 Results and discussion

3.3.1 Characterization of the Ga-doped ZnMgO nanowires

Figure 3.1 SEM images of the Ga-doped ZnMgO nanowires grown by (a-b) 7200 pulses and (c-d) 36000 pulses with various magnifications. The inset in (d) highlights the sidewall of the nanowires. The length of the scale bar is 100 nm.

The morphology of the Ga-doped ZnMgO nanowires are displayed in Figure 3.1. Most nanowires grew perpendicular to the sapphire substrates with an average diameter around 100 nm. We could clearly observe some nanobelts scattered within the nanowires array and the wires were in lack of hexagonal shape. The side wall of the nanowires exhibited zigzag morphology, which indicated the change of growing dynamics after incorporation Ga and Mg simultaneously.

Figure 3.2 XRD and XPS characterization of the Ga:ZnMgO NWs (36000 Pulses). (a-b) Element Scan of the Ga and Mg. (c) XRD pattern of the NWs, both the experimental data and the standard pattern are display in square root scale.

To figure out whether the nanowires were crystallized or amorphous, XRD were conducted and the results were displayed in Figure 3.2. The dominating peak was assigned to the (002) plane, which indicated that the wires grew preferentially along the c-axis. The peak appeared at 35.46° was assigned to the (101) plane. The appearance of this peak was probably due to the lateral growth of nanorod at the base of each nanowire, which was common in the buffer layer assisted nanowire growth. The lattice parameter could be extracted from the diffraction peak position by simple Bragg's law and the results were compared with the standard refraction pattern of ZnO powder shown in the Table 3.1.

	c (Å)	a (Å)
Experimental	5.3094	3.3260
Standard PDF	5.2066	3.2498

Table 3.1 Comparison between the experimental lattice constants with the standard lattice parameters

The lattice spacing in both a and c axis was enlarged in the synthesized nanowires. Considering the nanowires were annealed for 30 min at elevated temperature and the doping atoms were both smaller than the zinc, it is reasonable to owe this phenomenon to the excess metallic zinc incorporated in the lattice. Also, the Ga and Mg element were both resolved in Figure 3.2a and b respectively, indicating the successful incorporation⁴⁰.

To justify the viability of tuning the energy band gap via Mg alloying, LTPL from 10-300 K was conducted and the results were compared with the undoped ZnO grown in similar conditions. As shown in Figure 3.3a, the NBE region of the doped ZnMgO nanowire was dominated by a featureless broad peak. The broadening was caused by the distortion of the periodic potential induced by the extrinsic atoms. At 10 K, the peak position was around 3.43 eV, confirming the Mg doping enlarged the energy band gap by at least 0.07 eV¹⁴². At 300 K, this blue-shift was even larger. It was obvious that the DLE in the Ga:MgZnO NWs was suppressed compared to the undoped samples. That was possibility caused by the significant depletion effect induced by high electron concentration^{101, 143-145}

Figure 3.3 (a) 10 K and 300 K PL comparison (b) 10-300 K LTPL of Ga:ZnMgO NWs and the inset was the Varshni equation fitting of the peak energy positions.

As for the blue-shift of the Ga-doped ZnMgO nanowires, we deduced that the reason should be Mg alloying. Although the Burstein-Moss effect induced by Ga doping could also enlarge the band gap, it would manifest itself in the absorption spectra rather than PL emission according to the Kawasaki's research¹⁴⁶. The dominant radiative recombination route in n-type doped materials would be donor-to-free-hole or DAP transitions, which has lower energy than the ZnO free exciton recombination (3.37 eV). In our PL spectra of Ga:ZnMgO, the center of the dominant peak is around 3.43 eV. Thus, we could deduce that the blue-shift of PL was caused by Mg alloying.

The 0.07 eV shift was calculated as follows. At 10 K, the dominant transition of Ga:ZnMgO should be donor bound exciton (D^0X). The energy of D^0X transition could be expressed as¹⁴⁷:

$$E_{DX} = E_g - E_X - E_{local}$$

In this equation, E_{DX} , E_X , and E_{local} denote donor-bound-exciton energy, exciton binding energy and localization energy of excitons at Ga dopant sites. Thus, the E_g could be written as:

$$E_g = E_X + E_{DX} + E_{local}$$

E_{DX} was measured to be 3.43 eV with E_X and E_{local} equal to 0.06 eV and 0.016 eV.¹⁴⁷ In comparison with the band gap of ZnO, the energy band gap of Ga:ZnMgO is 0.07 eV larger.

In order to explore the nature of the emission peak, the Varshni equation was utilized to fit the peak position (10-120 K) changing with the increasing temperature and extrapolated to the 300 K⁴. The equation was shown as follows.

$$E(T) = E(0) - \frac{AT^2}{B + T}$$

In this equation, the $E(T)$ and $E(0)$ denote the energetic positions of an optical transition at temperature of T and 0 K. A and B are both constants. Herein, we use the 920 K as the value of B from the reference. The fitting results were summarized in the table below.

Fitting Parameters	Value	Standard Error
$E(0)$ (eV)	3.41957	0.00133
A (eV/K)	0.00148	1.59071E-4
B (K)	920	0

Table 3.2 Fitting parameters of the Varshni equation of DX peaks of Ga:ZnMgO

Due to the high concentration of the Ga doping, the dominant peak should originate from donor bound exciton recombination. However, the experimental data deviated obviously from the Varshini fitting at the low-temperature end of the curve (10 - 40 K), it indicates there may exist a switching between two D^0X peaks created from two types of donors with different exciton binding energy. With the increasing temperature, the exciton would dissociate from the shallow trapping to the deeper trapping without the appearance of the free-exciton peak.

As an important application, optically pumped single-NW lasing was demonstrated in the following Figure 3.4. The single NW was pumped by the 266 nm nanosecond laser with step-increasing power and the spectra were collected by micro-PL with X100 magnification. At the low pumping region, only very weak spontaneous emission could be collected by the CCD due to the limited emission from single nanowire. After the threshold was reached at 0.6 μ J, the PL intensity exhibited a superlinear relationship on

the pumping intensity and quickly saturated at 2.5 uJ. The inset in Figure 3.4b was the dark-field optical image of the lasing NW and the bright spots were caused by scattering of the lasing emission. From the ring-like pattern at the end facet together with periodic bright spots, we could infer that the nanowire lasing feedback was provided by the Fabry-Perot cavity^{148, 149}. Moreover, we could estimate the NW length to be 18.3 um with 1.3 um circumscribe diameter.

Figure 3.4 (a) Power-dependent PL spectra of single Ga:ZnMgO NW (b) Integrated PL intensity dependence on the pumping Power. The selected integration range was from 371-408 nm. The inset was the optical image of the lasing individual nanowire

Figure 3.5 Detailed comparison of three lasing spectra when the pumping intensity equals to 1.2, 2.7 and 4.2 uJ.

To investigate the nature of this laser cavity, we performed a comparative calculation between the whisper gallery mode (WGM) and Fabry-Perot (F-P) cavity^{53, 150, 151}. From the unchanged peak position of different modes with increasing pumping intensity as shown in figure 3.5, we should rule out the possibility of random lasing. Thus based on the geometric data we obtained from the microscope image, the theoretical quality factor (Q) and free spectral range (FSR) were shown below.

$$\text{FSR(WGM)} = \frac{\lambda^2}{n\pi D} \quad \text{FSR (FP)} = \frac{\lambda^2}{2nL}$$

$$Q(\text{WGM}) = \frac{\pi D m n R^{\frac{m}{6}}}{2\lambda \left(1 - R^{\frac{m}{2}}\right)} \sin \frac{2\pi}{m} \quad Q(\text{FP}) = \frac{2\pi n L}{\lambda(1 - R)}$$

Herein, the n , λ , m , L , D and R refer to the refractive index, wavelength, polygon order, cavity length, cavity circumscribed diameter and reflectivity of nanowires, respectively. We insert the refractive index value of 2.5 and geometric data of nanowires into the equations and found that the lasing feedback was not likely caused

by WGM. Considering the limited diameter of the nanowire, the lasing Q would be very low with a very sparse distribution of the modes (calculated to be 18 nm) for lateral WGM. A detailed calculation regarding F-P cavity was performed and Q was calculated to be 930 with the R assumed to be 0.2, which was a reasonable value for the nanowire end facets. Meanwhile, the FSR could be calculated to be around 1.6 nm and it fitted well with the 3 strongest peaks in the shorter wavelength. As have been shown in the SEM images, the nanowire possessed two facets not strictly parallel. The wire-substrate facet was flat, which corresponds to the left side in the optical image while the top tips of the NWs were sharp, resulting in the overlapping of two sets of lasing modes forming from cavities with various optical path length.

On the other hand, we could observe an anomalous blue-shift in the lasing modes with the increased pumping intensity. That was caused by the interplay of the gain spectrum blue-shift due to the Botstein-Moss effect as well as the decrease refractive index caused by the high pumping intensity¹⁵². The joint action would result in the blue-shift in both the modes as well as the gain.

Center wavelength	FWHM	Q
384.05359 *	0.35243	1089.73013
384.73967	0.39988	962.137816
385.57265 *	0.38102	1011.94859
386.56007	0.51355	752.72139
387.30801*	0.45379	853.496133
388.35337	0.62913	617.286364
389.3246	0.55644	699.670405
390.22736	0.65236	598.177939
391.03818	0.43309	902.902815
392.09838	0.42075	931.903458
393.11301	0.42614	922.497325
394.3032	0.40447	974.863896
395.29143	0.38708	1021.21378

Table 3.2 Gaussian fitted peak position and Q of various lasing modes shown in Figure 3.5

3.3.2 Characterization of P-doped ZnMgO Nanowires

P-doped ZnMgO NWs have seldom been demonstrated and their related growth mechanism in PLD was rarely studied before. So we conducted a series of experiments to explore the optimized growth conditions. As have been mentioned in chapter 1 & 2, the most common modulation factors in PLD are the background gas species and pressure. To suppress the oxygen deficiency formation and increase the growth anisotropy, O₂ and Ar were injected into the chamber in a mixture^{94, 153}. Their mixing ratio and the total pressure were chosen as the variables to be studied and the results were shown in Figure 3.6 and 3.7.

Figure 3.6 The morphology of nominal P:ZnMgO NWs grown in the certain mixture of O₂/Ar. (b) 28 Pa O₂ / 10000 Pa Ar (c) 56 Pa O₂ / 10000 Pa Ar (d) 28 Pa O₂ / 1008 Pa Ar. Their PL spectra were shown in the (a) with the line color corresponds to the fake color of their SEM images. The insets in SEM are the morphology of the products at the edge of the substrates where the plasma could seldom reach.

Several reports focused on the respective role played by the aforementioned two kinds of gas. Ar was monoatomic molecular gas, which possesses larger mass than the both the Mg and P. So their impingement would slow down the species in the energetic plasma and significantly favor the anisotropic growth free of dopants. On the other hand, the oxygen was highly reactive and would feasibly react to the Mg, P and Zn to form tiny droplets. These droplets acted as the small reactors similar to the Au catalyst in the VLS growth mode once reach the substrate. Moreover, the existence of excess O₂ would

considerably suppress the formation of *n-type* defects, namely the V_O , mitigating the background carriers in the NWs¹⁵⁴⁻¹⁵⁶.

As shown in Figure 3.6, we first tried to optimize the ratio between O_2 and Ar. At the extremely high Ar pressure, NWs exhibited high aspect ratio and their PL seemed like the spectra of undoped samples based on the absence of both blue-shift and defect-induced DLE. After all, the high concentration of Ar would scatter the dopants away. Meanwhile, once we increase the oxygen ratio even without changing the partial pressure, the produced NWs exhibited dissimilar optical properties. The blue-shifted PL proved the incorporation of the Mg and the low NBE/DLE ratio was caused by the inferior crystal quality introduced by exotic atoms. The PL characterization details were generalized in the table 3.3.

BG Pressure: $P(O_2)/P(Ar)$	FWHM (meV)	Peak Position (eV)
28 Pa/ 1008 Pa	159	3.360 eV
56 Pa/ 1008 Pa	208	3.347 eV
28 Pa/ 10000 Pa	113	3.268 eV

Table 3.3 The peak position and optical quality (FWHM) comparison of samples in Figure 3.6 (a).

After a series of optimization, we found that the O₂/Ar ratio around 1:6 could produce nanowires with a balanced optical property and doping concentration. And then, we continued to look for the most appropriate total pressure as displayed in Figure

Figure 3.7 The morphology of nominal P:ZnMgO NWs grown in different total pressure of the Ar/O₂ 6:1 gas mixture.

With lower total pressure, the NWs displayed much lower aspect ratio and larger degree of randomness in the growth orientation. However, though the NWs in figure 3.7a exhibited satisfactory morphology with minimum cross-links between the wires, the incorporation of Mg and P was too poor to be detected by XPS. The detailed composition and optical characterization of this set of wires was shown in Figure 3.8. So we found that the 240 Pa/ 1440 Pa O₂/Ar mixture was the closest to the optimized

point for P:ZnMgO NWs growth, taking into account the trade-off between the XPS and PL results. The XPS results revealed that the atomic concentration P and Mg under that condition was 10.58 % and 5.69 %, respectively.

Figure 3.8 XRD pattern of the P:ZnMgO NWs and the following table was the lattice parameter comparison chart between our sample and the standard PDF card.

The crystalline characterization results were shown in Figure 3.8. From the direct inspection of the SEM images, it seemed the nanowires were randomly oriented with deteriorated crystal quality^{2, 96, 157, 158}. Yet, only two strong peaks dominated the whole pattern, indicating randomness actually originated from the hierarchical branched structure of NWs. The calculated d-spacing in the inset chart shown that the c-axis contracted whereas the a-axis expanded in the P:ZnMgO NWs. That could be explained by coulomb interaction between the negatively charged ionized P acceptor and Zn positive ion¹⁵⁹.

Figure 3.9 PL spectra of samples grown using different oxygen partial pressure. The inset is the atomic concentration of the Zn, Mg, P of the samples.

To further characterize the P acceptor state in the ZnMgO NWs, LTPL was conducted and the results were shown in Figure 3.9. The free exciton (FX) peak manifested itself as a shoulder at the higher-energy side of the D^0X with the transition energy equal to 3.514 eV. Compared to the 3.37 eV energy of FX in undoped ZnO, it blue-shifted 144 meV. The peak beside the FX was assigned to D^0X due to the small localization energy (only 28 meV).

Figure 3.10 Temperature-dependent PL of P:ZnMgO NWs from 10-300 K

The dominant peak in the PL spectra was assigned to the donor-acceptor-pair (DAP) transition due to two reasons^{54, 160, 161}. On one hand, its intensity quenched very rapidly with the increasing temperature due to the increasing ionization degree of shallow donors. On the other hand, the peak position blue-shifted with the increasing temperature, indicating a transition from DAP to free-to-bound transition (eA^0)^{162, 163}. On the lower energy side of the sharp DAP peak; at least two orders of its longitudinal phonon replicas (DAP-nLO) were clearly resolved. The existence of discernible multiple LO-phonon replicas indicates the satisfactory crystal quality of the sample. Between the FX and the DAP, laid the A^0X and D^0X transition lines, respectively. The A^0X were more tolerant to the thermal quenching compared to D^0X owing to the larger localization energy.

It is noteworthy to mention that there should be one/multiple “shallower donor” state(s) than the state presented in the D^0X peak. This hypothesis originated from the observation of the rapid drop in the DAP intensity together with the anomalous intensity fluctuations of both A^0X and D^0X occurred in 10-30 K range. Herein, the reason of rapid DAP intensity drop was suspected to be the partial ionization of the “shallower donor”. Meanwhile, according to the Hayne’s rule in ZnO, the localization energy could be estimated to be one-quarter of the donor binding (ionization) energy. Thus, this “shallower donor” would feasibly release the trapped excitons even at low temperature and the released excitons were again trapped at the A^0X and D^0X states. Due to the high incorporation concentration of P and its large localization energy, the A^0X and eA^0 emission dominated the room-temperature PL.

To confirm the *p-type* conductivity of the NWs array, diode structure was fabricated based on the P:ZnMgO NWs/*n*-ZnO thin film junction. The contact was formed by e-beam evaporation of Ni/Au on the NWs and Ti/Au on ZnO thin film^{164, 165}. The device schematic as well as the I-V curves was shown in the following Figure 3.11. We could observe that the good ohmic contact was formed both on NWs and thin film. The relatively larger current between *p*-type contacts than between *n*-type contacts was caused by the much shorter distance between the *p*-contacts, as well as the thicker conductive layer (compared to only 100 nm thick ZnO thin film). It could rule out the possibility of contact-induced rectification. An ideal *p-n* junction curve was used to fit the experimental I-V data and the obvious rectification behavior was observed. This indicates that we successful achieved *p-type* ZnMgO NWs by heavy P doping. The fitting equation and parameters are listed as follows.

$$I(V) = I_0[\exp\left(\frac{V}{\eta V_T}\right) - 1]; \quad V_T = \frac{k_b T}{e}$$

Herein, the fitting results showed that $\eta V_T = 2.54 \pm 0.14$ (V) and $I_0 = 0.482 \pm 0.0576$ mA. Thus, the ideality factor η was calculated to be 97.99, which was caused by the deep-level-assisted tunneling of carriers.¹⁶⁶

Figure 3.11 (a) I-V characteristics of P:ZnMgO NWs/n-ZnO thin film diode. The inset figures were the I-V curves of two metallic contacts and the device schematic. (b) Energy band diagram of the ZnO/P: MgZnO p-n junction.

3.4 Conclusions

In this chapter, we have successfully demonstrated the *n*- and *p*-type doping of the MgZnO alloyed NWs/Nanostructures. The incorporation of Mg has successfully tuned the energy band gap. Though the LTPL of Ga:ZnMgO exhibited the featureless broad peak in NBE region, its optical property was still excellent revealed by the low threshold optically pumped lasing. On the other hand, the LTPL of the P:ZnMgO displayed large band gap blue-shift with strong acceptor related peaks clearly resolved. The multiple orders of phonon replicas indicated the NWs possessed good crystal quality. In the fabricated diode junction with *n*-ZnO thin film, *p*-type conductivity was proved to exist by rectification behavior^{49, 167}.

Chapter 4. Spatially Tailoring the band structure via surface doping to manipulate optical properties of ZnO

Nanowires

4.1 Introduction

As have been introduced previously, ZnO nanowires trigger remarkable research favor towards UV optoelectronics such as NW-lasers, NW-LED and NW PDs.^{60, 168-171} In spite of the viability of realizing low-threshold excitonic lasing,¹⁷² NWs array is an advantageous platform providing enhanced confinement of light, which is favorable for realization of compact lasers.¹⁷³ However, the high surface-to-volume ratio (Sa/Vol), which is an intrinsic trait of nanomaterial, extremely depreciates optoelectronic performance of NWs. The detrimental influence could be generalized into two aspects. One is the band bending effect induced by surface adsorbed ionized gas (such as O_2^- and CO_3^{2-}), which would dissociate the exciton into spatially separated electrons and holes.¹⁷⁴ The other lies in the high density of surface states caused by defects and dangling bonds, giving rise to the non-radiative (NR) decay and DLE.^{102, 175, 176}

Except for the Sa/Vol problem, the doping required for fabricating high-performance optoelectronics would also deteriorate the optical properties of NWs somehow.⁴⁰ While able to introduce extrinsic carriers, dopants would also induce structure defects and lattice strain, diminishing probability of NBE.¹⁷⁷

Being widely disregarded, doping itself could as well tune the alignment of band gap, which we could recall from the *p-n* junction band alignment in the depletion region.^{108, 171} Compared to widely utilized surface passivation methodology where materials with higher band gap are coated onto nanowires (usually MgO for ZnO) to

increase NBE/DLE in PL, tailoring electronic band structure via doping is advantageous in the way that people could get rid of usage of lattice-mismatch material with low conductivity by which EL properties would be somewhat be weakened.¹⁷⁸ Moreover, materials with wider band gap usually possessed smaller refractive index. As a result, light extraction would be obstructed in coated structures. Thus, to simultaneously enhance the carrier density and optical property is the key significance of this strategy. On one hand, the doped shell enhances the carrier concentration while maintains the crystalline. On the hand, spatially tailored band gap mitigates the radial out drifting of holes, increasing the NBE/DLE ratio and extenuating the non-radiative recombination between free holes and the captured carriers. Moreover, research regarding spatially modulating the band through doping has been seldom published to the best of our knowledge.

In this work, we performed the aforementioned band gap modulation scheme as well confirmed the optical property enhancement through systematically analyze the LTPL. Moreover, the XPS measurement of the oxygen valence states further supported our proposed band tuning model.

4.2 Experimental Process

4.2.1 Synthesis of ZnO/Ga:ZnO Core-shell nanowires

Figure 4.1 Growth Schematic of the core-shell ZnO-Ga:ZnO nanowire. The green denotes undoped ZnO while the blue denotes the Ga-doped shells.

The growth contains two phases. In the first phase, ZnO NWs were self-assembled on *p-GaN* substrate via hydrothermal route using the procedure described in chapter 2. To grow nanowires with various diameters and pick the set with proper NBE/DLE ratio, 25 mM, 35 mM and 50 mM concentration of precursor solutions were used. As for the second phase, doped shell was epitaxially grown by PLD on the nanowires produced in the previous phase. Prior to coating, ZnO NWs were annealed at 700 °C in oxygen flow (3.5 Pa, 50 SCCM, balanced by the gate valve) in the PLD chamber for 40 min to improve the crystalline and remove the surface contaminations for successive phase. Then, Ga:ZnO shell (c.a. 2% atomic concentration of gallium) with various thicknesses was grown at 800 °C with 300 mJ laser pulses using the same background gas condition

in annealing. Then sample is cooled down using the procedure as described in Chapter 2.

4.2.2 Comparative characterization of the NWs

As-grown ZnO NWs and core-shell NWs are comparatively studied by SEM, TEM, EDX, XPS, RTPL as well as LTPL. All the samples in the XPS characterization were synthesized from the same batch of hydrothermal-PLD growth procedure. In addition, they were all stored in the same dry box for one day before they were characterized by XPS to ensure the comparability of their results.

4.3 Results and discussions

Figure 4.2 (a) SEM of the hydrothermal as-grown NWs (sample synthesized from 35 mM precursor), of which was zoomed in (b). (c) SEM of as-annealed NWs and then they were deposited with around 10 nm-thick Ga-doped ZnO, shown in (d).

Figure 4.2 showed an evolutionary modification of morphology during the annealing and shell deposition process. The sample in-test here and in the following parts was synthesized using 35 mM precursor, if without further notification, Figure 4.2 (a-b) displayed that these dense-packed NWs formed an array with c-axis perpendicular to substrate via self-assembly. The hexagonal shape indicated that the wires possessed fairly good degree of crystalline, which could act as excellent “templates” for the on-grown shell. The mean radius of NWs was measured to be around 180 nm with the aspect ratio ranging from 5 to 20.

For the sake of trustworthiness of the proposed surface doping strategy and to preclude the occurrence of complete carrier depletion, NWs with different radius were

synthesized through controlling the precursor concentration. As shown in Figure 4.3, annealing procedure induced tiny pits at the surface of the ZnO NWs. The phenomenon was caused by relocation of surface atoms and agglomerated V_o .¹⁰¹ After the shell deposition (around 10 nm), the amount of little holes decreased and the NW surface was smoothened, shown in Figure 4.3d. This figure also shown the uniformity of diameter along the axial direction of the wire, confirming there didn't exist shadow effect.¹⁰¹

Figure 4.3 Average diameter of the undoped ZnO nanorods vs. the precursor concentration. The error bar denotes the standard deviation from the center value. Over 150 randomly picked nanorods are counted to generate each data point displayed in this figure to guarantee the measurement is statistically significant

HRTEM results are shown in Figure 4.4 to better resolve the epitaxial relationship between the core and shell as well as measure the lattice constant for the Ga:ZnO shell. Figure 4.4a and b showed that the Ga:ZnO shell is uniformly deposited along the nanowires and the interface between core and shell could be clearly resolved. Herein,

we use 200-pulse-deposited sample (thicker shell) rather than the 100-pulse-deposited sample in the SEM to facilitate unequivocal imaging and data explanation. Directly measured from Figure 4.4b, the shell thickness reached 16.7 nm, very close to the estimated 20 nm thickness via linear fitting of thickness vs. deposition pulses using a series of Ga:ZnO thin-film samples as reference. In this chapter, we would use the nominal thickness to nominate samples for the ease of discussion, as well as relating the characterization results with the growth procedure better. SAED in Figure 4.4d confirmed the existence of only one set of diffraction spots in the reciprocal space with direction vector labeled, showing the wires growing along c-axis. More importantly, it supported the argument that the doped shell grown epitaxially on the hydrothermal-synthesized nanowires.¹⁷⁹

Figure 4.4 (a) TEM image of one core-shell wire with its core-shell interface clearly resolved in (b). (c) SAED of the core-shell nanowire (c).

For the straightforwardness of inspecting the lattice fringe, HRTEM is conducted as shown in Figure 4.5. The shell was highly crystallized rather than amorphous and the d-spacing was measured to be 0.271 nm from the Fast Fourier Transform (FFT) of the image as shown in the inset. Moreover, the existence of the Ga dopant in the shell could be proved by comprehensive analysis of the EDX (shown in Figure 4.6) together with the LTPL results.

Figure 4.5 HRTEM of the Ga:ZnO shell and its FFT image are shown in the inset. The bar in the inset denotes 5 nm^{-1} . The white square in the TEM is the region of interest (ROI) for FFT operation.

Figure 4.6 EDX measurement of a single core-shell nanowire under TEM.

EDX results here demonstrated the element mapping of the Zn, O, Ga along a single nanowire. However, due to the Ga concentration was too low considering that it only resided in the doped shell, EDX could not provide the accurate concentration. However, in the following LTPL measurement, the characteristic peak appeared which confirmed the incorporation of the Ga.

After the doped shell was epitaxially deposited, the enhanced optical property of the wires manifested itself through the intensified NBE, as displayed in the RTPL measurement (**Figure 4.7**). For the samples with different shell thickness, they didn't exhibit unidirectional peak shift, implying the sample optical enhancement was not due to the shell luminescence or other extrinsic effects such as annealing.

Figure 4.7 PL of core-shell samples with the influence of shell thickness and core diameter to be studied. (a) NBE and (b) normalized PL of core-shell samples with different shell thicknesses. c) The relationship between DLE/NBE on NW diameter of as-annealed core-only sample and 10 nm core-shell samples.

The NBE of the 20 nm-shell sample experienced 100 % enhancement and absence of dependent relationship between the NBE enhancement and the shell thickness further exclude the interference from shell induced PL. We should declare that the four samples in comparison were synthesized and processed in the same batch to guarantee the comparability. Figure 4.7b showed that the NBE/DLE ratio was increased by at least one fold for the surface doped samples, supporting the proposed theory that doped shell could mitigate the probability of surface-related DLE and nonradiative recombination. Through cautious inspection of the DLE, we found that the all DLE peaks red-shifted compared to the as-annealed sample, suggesting that the doped shell modifies the likelihood of various defect-center-related emission. The origins of the NBE enhancement and modulation of DLE will be elaborated based on a complementary explanation of LTPL and XPS results.

Figure 4.8 10 K PL spectra of the core-shell nanowire and as-annealed sample.

LTPL at 10 K of as-annealed and core-shell sample was measured and shown in figure 4.8 using the set-up shown in Chapter 2. Their intensities were shifted for clear comparison and we only focused on the NBE temporarily. Both PL spectra exhibited asymmetric peak consisting of fine features. As for the annealed ZnO NWs nanorods, the dominant peak at 3.356 eV was tentatively allocated to exciton bound to neutral donor (D^0X), accompanied by their longitudinal optical replicas at 3.290 and 3.217 eV.⁷³ The empirical Varshni equation fitting from 10-140 K (extrapolated to 300 K) shown in Figure 4.9 confirmed our designation of D^0X was valid, both according to its peak position and its temperature dependent behavior.¹⁸⁰ Additionally, the appearance of unambiguous two order of phonon replicas suggested the increased quality of crystalline during the annealing procedure. The evident relative broad shoulder at 3.331 eV was aligned to the Y-line. Its appearance was caused by the defect-induced exciton localization, more specifically, at defects near the NW surface.¹⁷¹ After all, nanowires possessed near defect-free crystal quality near the core. Thus, the Y-line could act as a gauge of the exciton bound to surface defects. Then, for the PL of GZnO:ZnO core-shell NWs, it differed from that of the as-annealed sample in two ways. On one hand, the intensity of Y-line largely decreased (log scale of the vertical axis), suggesting the trapping of excitons at surface defects was mitigated. On the other hand, two small peaks 3.312 and 3.236 eV appeared near the phonon replicas of D^0X . The two peaks were the two-electron-satellite (TES) induced by surface doped Ga according to peak position together with the extracted ionization energy.⁴⁰ Consistent with the effective mass theory (EMT), the donor ionization energy donor could be extracted from the energy spacing from D^0X and its TES the following equation.

$$E_D = E_{1s \rightarrow 2p} + \frac{1}{4} E_{D, EMT}$$

In this equation, $E_{D,EMT}$ denotes the theoretically calculated EMT donor Rydberg energy (56 meV according to Reference) and $E_{1s \rightarrow 2p}$ refers to the measured energy difference within D^0X and TES (42 meV from Figure 4.8). Thus, The donor ionization energy was calculated to be 56 meV, matching the literature reported experimental value very well and confirming the existence of gallium with the EDX data showed previously.⁴⁰

Figure 4.9. Varshini fitting of the energetic position of the dominant peaks of both samples, which shows that the nature of dominating peak is the donor-bound exciton in the low-temperature range. Considering the obvious thermal broadening effect, it is difficult to define the optical transition process from 200 K onwards.

Figure 4.10 Temperature-dependent DLE spectra of the (a) as-annealed and (c) core-shell nanowires with their broad peak decomposed into green and yellow components. The peak position and peak intensity are precisely extracted from gaussian fitting in (b) and (d). Herein, the DLE/NBE ratio refers to the DLE peak intensity normalized to the NBE intensity.

As shown in Figure 4.10 (a) and (c), the peak position regarding the DLE of these two samples both experienced manifest blue-shift from orange (2.1 eV) to green (2.4-2.5 eV) from 10 K to 300 K, which was unlike the common red-shift behavior of NBE because of lattice-contraction induced band gap renormalization^{60, 175}. Cautious study on the broad deep-level emission peak revealed that the abnormal large blue-shift originates from the competitive behavior between two distinct recombination channels. The first channel results in the yellow-orange emission 2.1 eV, namely the recombination from the conduction band (CB) to double-ionized oxygen vacancy V_O^{++} .

The second channel is the transition of electrons from single-ionized V_O^+ to the valence band (VB), associated with the 2.5 eV green band.¹⁰¹ Thus, the broad DLE spectra were decomposed as two Gaussians and their peak intensity and position were extracted by the best fitting as possible with all adjusted R^2 exceeding 99.9% shown in Figure 4.10 (b) and (d). The data points shown were all plotted with error bar indicating the standard deviation of fitting.

Figure 4.11 Comprehensive schematic band gap alignment taking into account the surface depletion and the defect center induced DLE emissions. The left side “air” denotes the surface side of nanowires. The probability of emission of different recombinations at various temperatures was modulated by a unified Fermi level.

In Figure 4.11 a and b, a comprehensive spatial band diagram was proposed elaborating on the enhanced NBE/DLE ratio as well as the modulated recombination probability at the two aforementioned DLE luminescence centers. As clearly displayed in figure 4.10 within 10-170 K, both the 2.1 eV and 2.5 eV components of the two samples exhibited rise in relative intensity induced by increased exciton-capture probability at oxygen vacancy sites. As the temperature approached 200 K, the relative intensity of orange peak decreased whereas the green peak increased. As have been demonstrated by

Simpkins et al,¹⁰² thermal induced increase in the carrier concentration throughout the wires would facilitate the augmentation of surface barrier height in this temperature regime. Consequently, the lateral built-in electric field was likely to remove one hole from V_O^{++} and generate more V_O^+ . According to our proposed band alignment model, that seemed as a reasonable mechanism of the wax-and-wane relationship between the green and yellow DLE components. Compared to the undoped sample, it was obvious that the yellow-orange peak of the Ga surface doped NWs declined at a higher temperature, indicating the built-in electric field induced the “well” in the band, mitigating the thermal deprivation processes of the yellow center.

When the temperature reached 250 K and beyond, the Fermi level of the NWs would be elevated higher than the energetic position of the V_O^+ , which made the green center easily quenched by the high concentration delocalized electrons. Thus, the Fermi level of the undoped core could be around V_O^+ at 300 K, scilicet, Fermi level was 0.8 eV more than the mid of the CB and VB, which was consistent with considering the natural *n-type* of intrinsic core as well the diffused carriers from heavily doped shell.¹⁸¹ From 250-300 K, the core-shell sample exhibited a more evident drop in SLE intensity than the as-annealed sample, which suggested that higher concentration of electrons in the surface doped samples quench the oxygen vacancies more effectively.

It is noteworthy that the doping-induced well in electronic band would also facilitate NBE. In the undoped wires, surface depletion effect would introduce the slope in the band gap as shown in Figure 4.11a, offering efficient yet detrimental nonradiative recombination route, which was schematically displayed as the red curved arrow for the guidance to your eyes^{61, 173}. The well, however, in our proposed doping scheme

mitigated the lateral diffusion of holes to the surface and thus suppresses the nonradiative recombination, meanwhile, it enhances the NBE.

Except for the carrier confinement effect induced by surface doping, XPS results (in Figure 4.12) revealed another favorable trait of the proposed structure, i.e. the reduction in surface adsorption. According to the Park's report, the elemental peak of oxygen of ZnO nanowires could be viewed as a combination of oxygen with various states, namely, oxygen in the lattice O_I (approximately 529 eV), defect related oxygen O_{II} (approximately 531 eV, referring to oxygen around oxygen vacancy, oxygen interstitials.) and adsorption oxygen O_{III} (around 533 eV).⁴⁰ As for all the surface doped NWs with different shell thickness, the adsorbed oxygen was all reduced and the 10 nm-shell sample exhibited the highest decrease by 50% compared to the as-annealed samples. The results are generalized in Figure 4.13 and this effect could be introduced by the doping-induced well which held both holes and electrons inside the nanowires, thus mitigating the adsorption (O_2^-) process. Yet, the underlying physics still needs further investigation.

Also, it is worthwhile to highlight that for the core-shell samples, they all exhibited higher defect oxygen concentration. That was due to the gallium dopant induced lattice distortion. However, it did not deteriorate the optical properties, further confirming the carriers were confined away from defective region.¹⁰²

Figure 4.12 Oxygen 1s XPS component comparison of a) the as-annealed and the core-shell samples with the shell thickness of b) 5 nm, c) 10 nm and d) 20 nm.

Figure 4.13, Normalized integrative intensity of O 1s components plot of the lattice oxygen, defect oxygen and surface oxygen. With the increasing shell thickness, the surface adsorbed oxygen decreases by 50%.

4.4 Conclusions

To conclude, we have suggested and demonstrated a novel and universal strategy to manipulate the nanowire optical properties via forming surface-doped core-shell structure. The growth of nanowire only involved hydrothermal method with a high product yield. Then the following PLD was well-established and scalable, which made this methodology feasible for various semiconductor nanostructures. By correlating the conjugating factors like carrier concentration, optical property, and surface depletion, this study provides a significant physical insight for designing high-performance optoelectronic nano devices.

Chapter 5. Excitonic energy recycling from ZnO defect states: towards electrically driven NW-QD hybrid white LEDs

5.1 Introduction

Since the emergence of colloidal quantum dots (QDs), there have been enduring research favors in developing inexpensive and solution-processable novel solid-state lighting (SSL) based on them^{182, 183}. Among the prospective utilizations in SSL, QD-empowered white light-emitting diodes have attracted tremendous attention^{184, 185}. In one aspect, traditional lighting devices are inefficient in converting electricity to light, e.g. incandescent bulbs and compact fluorescence lights (CFLs).⁹ The Energy Information Administration (EIA) of U.S. reported that 11 % of gross electricity nationwide had been consumed by lighting in 2014. Considering the display-related power consumption in rapidly booming personal digital products, this ratio would no doubt keep increasing. In contrast to high vacuum, elevated temperature and complicated equipment required by material fabrication in traditional semiconductor industry, QD synthesis is all solution-based reaction with accessible precursors, which is economically favorable.¹⁸⁶ The electronic structure engineering could be straightforwardly achieved by modulation of the diameter and composition. Status quo craves for w-LED, with the merits of high endurance and efficiency to revolutionize the lighting and display products. Due to their aforementioned favorable traits such as highly color purity and tunability, QDs are regarded as ideal lumophore in w-LEDs.¹⁸⁷

Though feasible in fabrication and band gap tuning, carrier injection to these organic-ligand passivated QDs is the major impediment towards commercialized

electrically driven w-LEDs. There are two routes to exciting quantum dots, including exciting QDs by blue or UV LEDs (PL route) and injection through configuration analogous to organic-LED (OLED) using charge transport layer (CTL) (EL route).¹⁸⁸ However, the EQE is fundamentally constrained by the EQE of back-lit LEDs. As for the EL excitation scheme, the inadequate conductivity of the polymer CTL together with the unbalanced carrier-injection renders prototypes show low EQE (~2%) and current densities.¹⁸⁷ Besides, majority of these archetypes merely apply single or few layers of QDs as the lumophore in order to assist carrier injection and mitigating the energy transfer and quenching between the layers.¹⁸⁹ The resultant low loading ratios of QDs, rigorously limits the device potential in high-luminescence applications. Furthermore, QD-based lighting necessitates the mixing of various dots or integration several red, green and blue (RGB) LEDs, hindering the on-going device miniaturization. To summarize, all-inorganic QDs energy injection schemes which could enable high loading and one-chip integration of QDs are greatly desired.

As have introduced previous, ZnO nanowires (NWs) have as well attracted significant attentions in the arena of short-wavelength optoelectronics.⁷⁰ The large surface-to-volume ratio introduces dangling bonds, surface adsorption and defects, resulting in significant exciton-trapping, visible DLE, and extra non-radiative channels. Hence, ZnO NW-based lighting devices thirst for delicate design to passivate the surface and recycle carriers/excitons from the defects.⁴

In this chapter, an innovative SSL device fabrication scheme is proposed. As shown in Figure 5.1, it incorporates CdSe quantum dots onto ZnO NWs surface in order to recycle the excitonic energy defect states and assist the excitation of QDs. Previous research in ZnO proved that nanowires could be treated as single crystal with low defect density in the core. As a result, it facilitates carriers transport due to the higher diffusion

length. From this perspective, ZnO NW is a high-performance CTL platform.¹⁹⁰ Besides, the NWs act as energy injection medium CdSe lumophores. The schematic of the band gap alignment is shown in Figure 5.1b. Herein, the fluorescence resonant energy transfer (FRET) from ZnO deep-levels to CdSe QDs not only excites the dots but also offers an alternative channel for trapped carriers, mitigating the nonradiative recombination near the NW surface. Furthermore, high surface to volume ratio of NW facilitates loading of QDs, which is promising in high-lumen w-LED applications. It is worthy to mention that all RGB lumophores are incorporated in single wire. Therefore, this design scheme facilitates the energy injection of one-chip integrated QD w-LED.

Figure 5.1 (a) GaN/ZnO/CdSe quantum dot white light-emitting-diode schematic. (b) The magnified single QD-coated microrods. (c) Band diagram depicting the idea of energy transfer from DLE of ZnO NRs to CdSe. Both in (b) and (c), the yellow curved arrows refer to the energy transfer procedure from rods to quantum dots.

5.2 Experimental Process

5.2.1 Synthesis of CdSe/ZnS core-shell colloidal quantum dots

The synthesis of colloidal CdSe/ZnS core-shell QDs was reported on a published literature.¹⁹¹ 1 mmol cadmium oxide (CdO, Sigma-Aldrich, 99.5%) and 2 mmol zinc acetate (Zn(Ac)₂, Sigma-Aldrich, 99.99%) were mixed with 5 mL oleic acid (OA, Sigma-Aldrich, 90%) in a 50 mL three-neck flask. The mixture was degassed in vacuum (around 3 Torr) at 120 °C for 2h. Then 25 mL 1-octadecene (1-ODE, Sigma-Aldrich, 90%) was added into the reaction vessel. The mixtures were then heated to 300 °C in argon. 0.2 mmol selenium (Se, Alfa Aesar, 99.999%) in 0.2 mL trioctylphosphine (TOP, Sigma-Aldrich, 90%) was injected into the flask rapidly. After 2 min 0.3 mL dodecanethiol was injected dropwise. The reaction was kept at 300 °C for 20 min, and then 2 mmol sulfur (S, Sigma-Aldrich, 99.998%) in 1 mL TOP was added. After 10 min, the reaction was ended by reducing the temperature.

5.2.2 Synthesis of ZnO NWs array

ZnO NWs are synthesized by hydrothermal reaction between zinc acetate and HMT precursors. The detailed methodology is similar to that in chapter 4 and an air-annealing procedure is conducted at 650 °C for 1h to eliminate the surface contamination.¹⁹²

5.2.3 Fabrication of hybrid w-LED:

CdSe quantum dots are directly spin-coated on the annealed nanorods array. After the solvent is dried, indium platelet and Ni/Au electrode is fabricated as *n*- and *p*-pad respectively. Indium electrode is formed using direct pressing whereas the Ni/Au electrode on *p*-GaN are formed using e-beam evaporation to get rid of damage of the QDs at elevated temperature.

5.2.4 Measurement and characterization

The morphology of the nanorods and the device are characterized using the field emission scanning electron microscope (Model JSM-6700F) and QDs diameter and morphology are measured in Transmission electron microscopy (Model JEOL 2010f). The steady-state PL is measured using a home-build PL system. The steady-state and transient PL are measured using the set-up in chapter 2.

5.3 Results and discussions

Figure 5.2 (a) SEM of as-synthesis ZnO NWs array. (b) ZnO NWs annealed in air for 1h. (d) Zoom-in of (b) exhibits small dimples at the rod surface. (c) X-ray diffraction of wires in (b).

The ZnO sub-micro/NWs array in this Chapter was self-assembled on commercial available Mg-doped GaN substrate via hydrothermal method shown in Figure 5.2, the average diameter of the NWs is around 800 nanometer with height around 4 micrometer. The highly uniform wire length favors the successive procedures such as spin-coating and electrode deposition. The wires exhibit hexagonal crystalline, indicating c-axis preferred growth and relatively high crystal quality.¹⁹² Subsequently, ZnO NWs are annealed in air to eliminate the surplus precursor attached to the wire surface. This circumstantial evidence of this argument is the increment of electron microscopy

imaging quality in Figure 5.2b and d compared to 5.2a due to removing of HMT. Also, it favors the unambiguous demo of the energy transfer process from defect levels to QDs by subduing the NBE and increasing the DLE. In figure 5.2c, XRD diffraction pattern of annealed wires further endorses this argument by showing the preferential orientation in (002) and (004) direction and absence of other diffraction peaks.¹⁹³ The annealing-induced dimples at the outer facets of the wires (in Figure 5.2b and c), which was possibly produced by the accretion of the oxygen vacancies and reorganization of superficial atoms.⁴

Figure 5.3 Aerial-view SEM annealed ZnO NWs (a) prior to QD coating and (b) after QD coating. (c) TEM images of CdSe/ZnS core-shell QDs with an inset showing the size distribution of the QDs (d) magnified view of image (c).

Afterward, QDs solution was spin-coated on the NWs. The average diameter of highly-uniform QDs was around 5.0 nm as displayed in the TEM images (Figure 5.3c and d), which enabled the quantum confinement of the excitons in CdSe (Bohr radius= 5.6 Å).¹⁹¹ Despite the fact that the size of QDs was beyond the SEM resolution, it is still relatively evident that the QDs solution filled the fissure in-between the wire and worsened the conductivity of the sample implicated by a much deteriorated imaging quality of Figure 5.3b compared to Figure 5.3a. Furthermore, this postulation is proved by the following I-V characterization (Figure 5.6).

Figure 5.4 (a) PL spectrum of air-annealed ZnO and the extinction spectra of QDs solution. (b) PL spectra of ZnO NWs and the integrated ZnO NWs/QDs.

The optical properties of the ZnO NWs and ZnO NWs/CdSe QDs were characterized by absorption and PL. In Figure 5.4a, the PL of the ZnO NWs exhibited two peaks, the NBE around 379 nm and a comparatively strong broad and featureless DLE peaking at 500 nm. The air-annealing mitigated NBE yet increased the DLE through generating deep-level states such as V_{Zn} and V_O .¹⁹⁴ It is obvious that DLE overlaps with the strong absorption range of the QDs to a large extent, which is critical for the fluorescence resonant energy transfer (FRET). After spin-coating of QDs, a narrow peak arose at around 625 nm in Figure 5.4b together with the declining DLE of the wires. Herein, The 625 nm emission was the radiative recombination of electron-hole pairs in QDs.¹⁹⁵ The PL quenching of the QDs was negligible in integration process with NWs. Allowing for the weaker intensity of the visible emission from wires than He-Cd laser, the major excitation source of QDs should be the 325 nm pumping laser. Nevertheless, the reduction in visible luminescence suggests that the FRET might be introduced by QDs, which has been verified in the subsequent transient PL measurement shown in figure 5.5.¹⁹⁶

Figure 5.5 Time-resolved PL (TRPL) of (a) ZnO NWs green emission and (b) QDs red emission, both individual and as an assembly.

To provide solid evidence for the existence of the FRET from the ZnO DLE to QDs, the transient PL spectrum of NWs and that of the NWs/QDs assembly were measured. As displayed in Figure 5.5, both TRPL exhibited single exponential decay and the lifetime of the uncoated NW DLE, as well as the QDs (solid), are extracted via fitting and results are shown in the legends in Figure 5.5a and b. After the assembly of the two materials is formed, the ZnO DLE lifetime is abbreviated while that of QDs is extended. This behavior was the concrete proof that FRET occurred in between these two lumophores. In the specific hybrid system, defect emission from zinc oxide donated energy to the attached QDs.¹⁹⁷ The FRET efficiency can be calculated from modification of donor recombination lifetime, namely ZnO green emission in our case, as shown in the following formula below.¹⁹⁸

$$\eta_{ET} = 1 - \tau/\tau_0 = 1 - 442 \text{ ns}/534 \text{ ns} = 17.07\%$$

The η_{ET} denotes the energy transfer efficacy in this equation. The τ and τ_0 denote donor PL lifetime when it coupled with the donor and as it is, respectively. Through inserting the measured data, FRET efficacy was calculated to be 17% round.

Trace back to the CdSe QDs employed, they were encapsulated by around 2.5 nm ZnS plus ligand according to the original report regarding this recipe.¹⁹¹ Thus, the spacing amid the NW and QDs was assumed to constrain the η_{ET} .

In order to further clarify this assumption, we tried to use the distance dependent FRET efficiency equation as follows to elaborate on the calculated results.

$$\eta_{ET} = \frac{R_0^6}{r^6 + R_0^6}$$

Herein, Förster distance and the donor-acceptor spacing are denoted by R_0 and r , respectively. According to Abhinandan's work,¹⁹⁹ the Förster distance in a dye-ZnO FRET process where the dye had a similar absorption coefficient and spectra overlapping was calculated to be 1.84 nm. Thus, it is rational to evaluate the R_0 in our system to have similar value. Substituting in the experimentally generated η_{ET} and 1.84 nm for the R_0 , then the r is calculated to be 2.4 nm. The value matched our TEM measured shell thickness very well, endorsing the assumption that constraints of the FRET efficiency originated from the ZnO-CdSe core spacing and self-consistently proved the presence of FRET.

Figure 5.6 I-V characteristics of the ZnO NWs matrix prior to and after integration with QD. The inset is the I-V curve of the Ni/Au eutectic p-contact on GaN.

To study the viability of this scheme, an archetype FRET-LED was fabricated straight based on the *p*-GaN/ZnO NWs/CdSe QDs configuration as displayed in Figure 5.1a. Favored by the uniform height of the NWs, the cathode of the device was fabricated by directly pressing the indium pad on top of the NWs array. The anode Ni/Au contacts on *p*-GaN were fabricated by electron beam evaporation. As displayed in the inset in Figure 5.6, the linear I-V characteristics confirmed the formation of ohmic contact, excluding the likelihood of Schottky contact-induced rectification behavior. I-V curves of both FRET-LED and the *p*-GaN/ZnO have shown rectification. Taking into account the voltage drop around the crossing point of ZnO/GaN and at the metal contacts, the turn-on voltage around 6.35 V of the FRET-LED was fairly close to the 3.3 eV electronic band gap of ZnO NWs.²⁰⁰ Under reverse bias, the somewhat high leakage current was most probably induced by the defects in the intermixing regions of

GaN/ZnO heterojunction.²⁰¹ These lattice-mismatch generated interfacial defects produce free carriers under reverse bias.¹¹³ Succeeding the coating of QDs, the leakage current was mitigated by surface passivation of NW surface together with the injected QDs which resided between the NW tips and In contacts.²⁰²

Figure 5.7 EL spectra of the (a) ZnO/GaN matrix heterojunction and (b) FRET LED under forward bias, respectively.

The EL of the *p*-GaN/ZnO NWs heterostructure and that of FRET w-LED were measured and the results are shown in Figure 5.7a and b. These two spectra were disintegrated into several peaks representing various recombination routes, which were generalized in the band alignment schematic of the FRET w-LED shown in Figure 5.8.

Figure 5.8 All-inclusive electronic band alignment of FRET w-LED.

In FRET w-LED, the short-wavelength blue component is primarily composed of the near-band-edge recombination in ZnO (~ 380 nm, purple arrow), ZnO/GaN interface-related emission (~ 410 nm, blue arrow) and the eA_0 (electron to neutral donor) related emission in GaN.²⁰³ The green part (~ 550 nm) and the red part (~ 625 nm) originate from DLE of ZnO and near-band-gap recombination of QDs, correspondingly. Herein, curled arrow between NWs and QDs represents the FRET. The electrically driven RGB builds up the matter-of-fact w-LED.

It is notable that the EL in sole GaN/ZnO NWs displays insufficient red component compared to the hybrid FRET LED. The origin of the small peak in orange (640 nm) relates to the recombination process concerning zinc and oxygen interstitial defects.²⁰⁴ The QD coating suppressed this transition thanks to the additional channel for carriers trapped at those defects.

Figure 5.9 CIE 1931 chromaticity coordinate of the (a) GaN/ZnO NWs and (b) the QDs FRET w-LED

According to the norms of Commission Internationale de L'Eclairage (CIE) 1931, the chromaticity coordinates of the *p*-GaN/ZnO NWs was calculated to be (0.322, 0.377) shown in Figure 5.9, which represented olive color. After formation of the FRET w-LED, the CIE value became (0.327, 0.330), fairly close to achromatic point (0.330, 0.330). The correlated color temperature (CCT) of the hybrid LED was calculated to be 5783 K according to the equation below, almost equal to the 5780K CCT of the sunlight.⁸ The natural sensation of the achromatic EL from FRET w-LED enables its utilization in indoor lighting. Moreover, the CCT could be feasibly tuned by changing the coated QDs species as well as alternating the annealing procedure of the nanowires.

$$\text{CCT} = 449n^3 + 3525n^2 + 6823.3n + 5520.33;$$

$$\text{in which, } n = (x + 0.3320)/(0.1858 - y)$$

It is noteworthy to emphasize that there may exist dual channels for energy injection into the CdSe QDs. The first channel is the aforementioned FRET whereas the other is the QD absorption of the short-wavelength region emission from the matrix. Thus, to differentiate the dominant channel for QD excitation is of great significance. Herein, we proposed that the short-wavelength emission from the matrix barely results in the emission, i.e. the FRET is the main channel. A schematic description of EL propagation supporting this argument is shown in Figure 5.10.

Figure 5.10 The schematic modeling the EL propagation in single ZnO NW, which is intersected in $(10\bar{1}0)$ plane.

Vanmaekelbergh et al¹⁶ reported that UV/blue and visible emission of ZnO were generated from two dissimilar recombination process. The NBE originated from recombination of excitons. In contrast, the DLE took place mostly adjacent to the outer surface of the wires.

Owing to the much higher electron mobility, it was inevitable that certain portion of NBE happened in the interfacial area at the nanowire bottom. However, we could expect that a large share of the emitted light coupled to the waveguide mode of the wires and transmitted towards top. Thanks to the high oscillator strength of excitons in ZnO, the NBE would couple intensely with the cavity excitons in ZnO NWs and

resulted in the uniform distribution of excitons along the axial direction. Meanwhile, generated mixture of excitons and photons would diffuse to the surface defect sites. This hypothesis is schematically demonstrated by the pinecone-shape distribution of NBE in Figure 5.10, considering the NBE to DLE transformation both in the transverse and longitudinal direction.

Inside the space where FRET could take place (c.a. 10 nm), the DLE is the predominant fluorescent process. Additionally, we applied QDs with 2 nm ZnS shell, which had a 3.54 eV gap at room temperature, higher than that of both ZnO and GaN.¹⁹¹ So the shell was unable to facilitate energy harvest from the NBE of ZnO. These characteristics guarantee that the excitation of CdSe quantum dots unambiguously originated from FRET.

Figure 5.11 The picture of the working hybrid CdSe QD-ZnO NW LED.

5.4. Conclusions

To sum up, an innovative device design scheme is proposed which excites the QDs by FRET from DLE of ZnO nanowires. The presence of FRET was proved through the comparative study on TRPL of the NW-QW assembly and η_{ET} is measured to be 17%. A prototype w-LED was fabricated to test the viability of the scheme. The EL of the device spectra exhibited CCT similar to the natural sunlight and achromatic white light-emitting-diodes have been achieved. This FRET LED functions well in atmosphere in absence of passivation polymer. It is noteworthy to elucidate that the CCT and RRB ratio could be feasibly tuned by several routes such as modulating the nanowires morphology and exchanging the QD types. Incorporation of versatile QDs with the semiconductor NWs family proposed in this research paves the way to next generation high brightness lighting with tunable color and lower power consumption.

Chapter 6. Conclusions and Outlooks

6.1 Conclusion

This thesis focused on the electronic band structure modulation of ZnO-based nanowires to find optimized balance between electrical and optical properties. As shown in Chapter 3-5, we have explored several ways to achieve this goal. We have achieved modulation of the electronic structure both by composition method (Mg incorporation) or spatially tuning of the carrier concentration. Moreover, utilizing the novel knowledge gained in chapter 3-4, we successfully demonstrate ZnO NW-based w-LEDs with color temperature similar to the sun.

6.1.1 Modulating the electronic structure via doping and alloying simultaneously

Carrier density, conduction type, and the electronic band gap were tuned simultaneously via synthesizing Ga and P-doped MgZnO NWs using PLD system. The blue-shift of spectra of these two types of wires verified the successful incorporation of Mg. Both the nanowire exhibited satisfactory optical properties. The Ga-doped wires exhibited lasing at 386 nm with a Q exceeding 1000. And the P-doped alloy NWs displayed two orders of LO phonon-replicas at low temperature, confirming the good degree of crystallization of such NWs with quaternary components

On the other hand, high concentration of P had successfully counterbalance the background free electrons and the prototype device showed *p-n* junction rectification behavior, confirming we have achieved the *p-type* conductivity.

6.1.2 Tuning the electronic band gap spatially to modulate the optical properties

We demonstrated the novel strategy of modulating the optical properties via surface doping of Ga and thus forming the ZnO/GaZnO core-structure. By systematical

analysis of the LTPL of both NBE and DLE emission, we confirmed that the doped shell not only confined the carriers away from the defective shell but also modulated the recombination probability of different DLE centers. Moreover, the proposed doping strategy together with the DLE decomposition methodology offered a novel paradigm in high-performance optoelectronic device design.

6.1.3 Excitonic energy recycling from ZnO defect states: towards electrically driven NW-QDs hybrid white LEDs.

Via incorporating CdSe QDs onto the NWs surface, QDs were excited by the recombination from carriers captured by deep-level states in electrically injected ZnO NWs for the first time. The device exhibited an achromatic emission with chromaticity coordinate (0.327, 0.330) and color temperature 5783 K, equal to the sun.

To sum up, the inner connections concerning my works are the material platform utilized, i.e. ZnO nanowires. I studied the underlying physics of three correlated aspects of the ZnO, namely, surface, optical properties and electronic band structure of the ZnO nanowires. As the result, this thesis contributed to the insights into ZnO nanowire synthesis and optoelectronics applications.

6.2 Outlooks

It has been over 17 years since the first demonstration optically pumped ZnO NW laser. Many researchers have discovered or already utilized feasible traits of ZnO for optoelectronic applications^{205, 206}. However, we must admit that there still seems a distance in between the lab and the final commercialization of ZnO NW-based devices^{174, 207-209}. The obstacles are widely acknowledged and a series of future works were still needed before we witness the day when ZnO could really replace the III-V semiconductor and lower the cost of blue LED significantly. From my perspective, the future endeavors on modulating the electronic band structure of ZnO includes but not limits to the following.

First, P:MgZnO NWs based devices may be an alternative to the *in-focus* N:ZnO NWs for their higher stability and band-gap tunability. After all, it has been studied by a few groups that the formation $P_{Zn-2V_{Zn}}$ was like to be responsible for the *p-type* conductivity of P-doped ZnO rather than P_O ^{33, 86}. Meanwhile, the Mg could also increase the V_{Zn} density. Their conjugating effect may produce *p-type* NWs with high concentration of acceptors and low ionization energy.

Second, forming the doped ZnMgO/ZnO core-shell wires, which are capable of confining the carriers as well as being highly conductive, may be a promising candidature in realizing the “true” NW-based electrically pump lasing, where the lasing happens in the NW rather than surface or NW/substrate interfaces.

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