

UNIVERSITY OF TECHNOLOGY SYDNEY



Doping and Characterisation of ZnO
Nanowires and Crystals

by

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A thesis submitted in partial fulfilment for the degree of
Doctor of Philosophy

in the

School of Mathematical and Physical Sciences
Faculty of Science

2015

Declaration of Authorship

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Abstract

ZnO is a wide bandgap semiconductor with a direct band gap of 3.37 eV and an exciton binding energy of 60 meV at room temperature. Due to their large band gap, high exciton binding energy and the ease of forming versatile low-dimensional nanostructures, ZnO nanowires have been widely studied for applications in optoelectronic devices. The lack of a reliable method for *p*-type doping and for controlling the *n*-type compensation limited to native defects in ZnO has hindered the development of ZnO-based devices. Group V elements, in particular nitrogen that has an ionic radius similar to that of oxygen, is widely believed to be a promising candidate for realising *p*-type doping in ZnO. In contrast, hydrogen, a common impurity in ZnO, can act as a shallow donor in ZnO. This project primarily aims to investigate the properties and behaviours of these two important impurities plus the native defects in both bulk and nanowire ZnO.

In this first part of the project, arrays of ZnO nanowires were fabricated using gold (Au) as catalyst. New insights into controlling nanowire merging phenomena were demonstrated in the growth of ZnO nanowires using monodispersed Au colloidal nanoparticles as catalysts. Both nanowire diameter and wire distribution density were found to be strongly dependent on the density of Au catalytic nanoparticles. Structural analysis and spectral cathodoluminescence imaging of the *c*-plane nanowire cross-sections revealed that thin isolated nanowires growing from the Au nanoparticles began to merge and coalesce with neighbouring nanowires to form larger nanowires when their separation is inferior to a certain threshold distance. The distribution of nanowire diameters and their green emission were found to be strongly dependent on the density of the Au nanoparticles. The merging phenomenon was attributed to electrostatic

interactions between polar nanowire tips during growth and well-described by a cantilever bending model.

The grown nanowires were subsequently doped with nitrogen by plasma annealing at 300°C. The chemical states of nitrogen dopants in ZnO nanowires and the optical properties of doped ZnO were studied by complementary chemical and optical techniques. It is found that nitrogen exists in multiple states: N_O , N_{Zn} and loosely bound N_2 molecule. The work establishes a direct link between a donor-acceptor pair (DAP) emission at 3.232 eV and the concentration of loosely bound N_2 . These results indicate that N_2 at Zn site is a potential candidate for producing a shallow acceptor state in N-doped ZnO.

Results are also reported on the electronic properties and kinetic behaviour of hydrogen dopants in bulk ZnO crystals. Hydrogen was found to be at the bond-centred site by forming O-H bonds after hydrogen plasma annealing. Hydrogen shallow donor and hydrogen bound to basal plane stacking faults (BSFs) are observed in the low-temperature high-resolution CL measurements of H-doped ZnO single crystals. Under the electron beam irradiation, hydrogen donors bound to BSFs dissociate from these defect sites and migrate to the periphery of the electron interaction volume. The hydrogen donors are confirmed to be in the $H_{BC, //}$ configuration by means of XANES measurements.

Acknowledgements

First and foremost, I would like to express my profound gratitude to my supervisors, Dr. Cuong Ton-That and Prof. Matthew Phillips, for the continuous support, advice and guidance during my study at University of Technology Sydney. They have provided me with the most enjoyable learning experiences throughout my time in Australia.

My sincere thanks also go to Geoff McCredie for his help with the construction of the nanowire growth system, Mark Berkahn for XRD measurements, Herbert Yuan and Katie McBean for daily technical support. I would also like to extend my thanks and appreciation to my fellow students Meng Huang, Mark Lockrey, Sumin Choi and Olivier Lee for assistance with cathodoluminescence characterisation and plasma processing.

I acknowledge the contributions of the UTS research team, led by Dr. Cuong Ton-That, that conducted measurements on ZnO samples at the Australian Synchrotron. This synchrotron work was assisted by beam line scientists, Bruce Cowie, Anton Tadich and Lars Thomsen.

Additionally, I would like to acknowledge the financial support from the UTS International Research Scholarship (IRS)-China Scholarship Council (CSC) PhD scholarships program.

Finally, I would like to express my heartfelt gratitude to my family. None of this would have been possible without the patience and understanding of my family.

List of Publications and Presentations

Journal papers

L. Zhu, C. Ton-That, and M. R. Phillips, Nitrogen incorporation in ZnO nanowires using N₂O dopant gas. *Mater. Lett.* **99**, 42-45 (2013).

L. Zhu, M. R. Phillips, and C. Ton-That, Coalescence of ZnO nanowires grown from monodispersed Au nanoparticles. *CrystEngComm* **17**, 4987 (2015).

C. Ton-That, L. Zhu, M. N. Lockrey, M. R. Phillips, B. C. C. Cowie, A. Tadich, L. Thomsen, S. Khachadorian, S. Schlichting, N. Jankowski, and A. Hoffmann, Molecular nitrogen acceptors in ZnO nanowires induced by nitrogen plasma annealing. *Phys. Rev. B* **92**, 024103 (2015).

S. Khachadorian, R. Gillen, C. Ton-That, L. Zhu, J. Maultzsch, M. R. Phillips, and A. Hoffmann, Revealing the origin of high-energy Raman local mode in nitrogen doped ZnO nanowires. *Phys. Status Solidi-Rapid Res. Lett.*, Accepted. In Press. DOI: 10.1002/pssr.201510405.

Oral Presentations at International Conferences

L. Zhu, M. Lockrey, C. Ton-That, and M. R. Phillips, Growth and optical properties of N-doped ZnO nanowires. APMC-10, ICONN 2012 & ACMM-22, Perth, February (2012).

L. Zhu, C. Ton-That, and M. R. Phillips, Au effect on the growth and optical properties of ZnO nanowires. AMAS XII – The Twelfth Biennial Symposium, Sydney, February (2013).

C. Ton-That, L. Zhu, M. R. Phillips, A. Tadich, L. Thomsen and B. Cowie.,
Nanocharacterisation of nitrogen dopants in ZnO nanowires. ACMM23 and
ICONN2014, Adelaide, February (2014).

Poster Presentations at Conferences and Workshops

L. Zhu, C. Ton-That, and M. R. Phillips, Nitrogen doping in ZnO nanowires using
N₂O dopant gas. ACMM23 and ICONN2014, Adelaide, February (2014).

L. Zhu, C. Ton-That, and M. R. Phillips, Nanocharacterisation of N-doped ZnO
nanowires. ANN Early Career Workshop, Sydney, July (2014) (The 2nd poster
award).

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Acronyms and abbreviations

AB	anti-bonding
A ⁰ X	neutral acceptor bound exciton
BC	bound-centre
BSF	basal plane stacking fault
CCD	charge coupled device
CL	cathodoluminescence
CVD	chemical vapour deposition
DAP	donor-acceptor pair
D ⁰ X	neutral donor bound exciton
ESR	electron spin resonance
FX	free exciton
LO	longitudinal optical
MOCVD	metal-organic chemical vapour deposition
NBE	near-band-edge
rf	radio frequency
SEM	scanning electron microscope
VLS	vapour-liquid-solid
VPT	vapour-phase-transport
VS	vapour-solid
XANES	X-ray absorption near-edge structure
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
WZ	wurtzite
ZB	zinc blende

Chapter 1 Introduction to ZnO Nanowires

Research on ZnO can date back to more than half-a-century ago [1]. Its unique properties have been gradually discovered, including strong piezoelectricity [2], high resistivity to irradiation damage [3] and stable room temperature lasing capability [4]. ZnO is a direct wide bandgap semiconductor with low raw material price and can easily form nanostructures. Compared with GaN, ZnO has larger exciton binding energy (60 meV for ZnO versus 25 meV for GaN); while the bandgap of ZnO is 3.37 eV at room temperature, only slightly smaller than the 3.39 eV bandgap of GaN [5, 6]. In addition, nanowires possess further exciting properties because of their large surface areas and short charge transport length. With the prosperity of nanotechnology in recent decades and the mature development of nitride-based optoelectronic devices, ZnO nanowires have been attracting increasing attention for novel applications, such as piezoelectric nanogenerators [7], ZnO nanostructure-based solar cells [8] and UV laser devices [9].

1.1 Motivation of the research

Mass-production and commercialisation of optoelectronic devices based nitride wide-bandgap semiconductors have been achieved, thanks to the development of specialised fabrication techniques that have enabled the routine growth of *p*-type nitride semiconductors with different doping levels [10]. Oxide based semiconductors is a promising alternative to nitride semiconductors given their potential capacity to

improve the performance of wide-bandgap semiconductor devices. In particular, ZnO, with unique optoelectronic properties, possesses several fundamental advantages over nitrides, has opened the door to a wide range of possible applications [11, 12]. Like its nitride counterparts, the benefits of ZnO can only be realised once a reliable *p*-doping method is established.

Semiconductor nanowires are pivotal for many nano-size functional devices such as photodetectors, lasers and transistors, where high surface sensitivity and dense integration are desired [13]. Chemical vapour deposition has this far achieved the most success in producing various types of ZnO nanostructures in large quantities via the Au-catalysed process, in which the catalytic Au seeding layer rapidly adsorbs metallic vapour and promotes orientated growth of nanowires [14, 15]. However, the growth of nanowires with precise control over dimensions and optoelectronic properties — a prerequisite for nanowire-based device applications — have not been achieved up to now. This project devises a new method of growing ZnO nanowires using monodisperse Au nanoparticles and provides an insight into the nanowire merging phenomenon. Although the merging of grown semiconductor nanowires has been observed previously [16], the interrelationships between the nanowire dimensions, defect structure and the catalytic Au nanoparticle concentration, are yet unknown.

1.2 Aims of the project

The main focus of this work is to investigate the ZnO nanowire growth mechanism and the behaviours of nitrogen and hydrogen dopants in ZnO. Firstly, aligned ZnO nanowires with controlled defect structures are required for studies of dopant behaviours. After obtaining the single crystalline ZnO nanowires via systematic

investigations of their growth conditions, nitrogen doping and related characterisations were carried out. The behaviours of hydrogen donors, which are commonly observed species in ZnO, were also studied.

The aims of this project can be summarised as:

- Develop a deeper understanding of the growth mechanism of ZnO nanowires using vapour transport method with Au as the catalyst.
- Determine the factors that govern the growth and defect formation in ZnO nanowires.
- Investigate the structural and optical properties of doped ZnO, especially the chemical and electronic states of nitrogen and hydrogen dopants that act as acceptors and donors in ZnO.
- Elucidate the electronic properties and kinetic behaviour of hydrogen in ZnO bulk crystals.

1.3 Thesis structure

This thesis focuses on the doping and characterisation of ZnO nanowires and single crystals. This thesis is structured as follows:

- Introduction on ZnO nanowires — Chapters 1 and 2.
- Experimental methods — Chapter 3.
- Main findings — Chapters 4, 5 and 6.
- Conclusions — Chapter 7.

Chapter 1 provides an overview of optoelectronic properties of ZnO and the main objectives of this project. In Chapter 2, a critical review on defect energy levels in ZnO

as well as the growth of ZnO nanowires, is given. Chapter 3 introduces the techniques and relevant instruments used for preparing the doped ZnO samples and characterising the structural and optical properties of ZnO nanowires and single crystals. In Chapter 4, the effects of various parameters on ZnO nanowires are investigated. A nanowire bending and coalescing model is established based on Euler-Bernoulli beam theory. Chapter 5 presents results from the *in-situ* and post-growth nitrogen doping of ZnO nanowires. Molecular nitrogen acceptors are identified in ZnO and its chemical states in ZnO lattice are reported. In Chapter 6, hydrogen incorporation and dissociation mechanisms in ZnO single crystals are presented. Hydrogen is found to be bonded to oxygen at the anti-bonding site and its trapping and detrapping mechanisms are investigated.

Chapter 2 Activities of Impurities and Native Defects in ZnO

Native defects and impurities play an important role in the optical and electrical properties of ZnO. This chapter provides an overview of structural defects and impurities in ZnO, with an emphasis on the current status of growing *p*-type ZnO by nitrogen doping.

2.1 Structural defects and impurities in ZnO

2.1.1 Point defects

As-grown ZnO, without intentional doping, is known to exhibit *n*-type conductivity. This intriguing behaviour has been attributed to the presence of intrinsic point defects, including oxygen vacancies (V_O), zinc interstitials (Zn_i), zinc vacancies (V_{Zn}) and antisites [Zn at O site (Zn_O) and O at Zn site (O_{Zn})], or impurities, such as Li, Na and Cu. These native point defects normally behave as donors and may compensate limited acceptors in the material, making it much easier to obtain *n*-type conducted ZnO than its *p*-type counterpart. Due to the partial deficiency in the material synthesis environment, the native point defects can exist in ZnO in a large number.

A summary of the formation energies of intrinsic defects in ZnO is presented in Figure 2.1. Under Zn-rich conditions, V_O and Zn_i has lower formation energies than O-rich conditions [17]. The defect concentration in an equilibrium condition has been

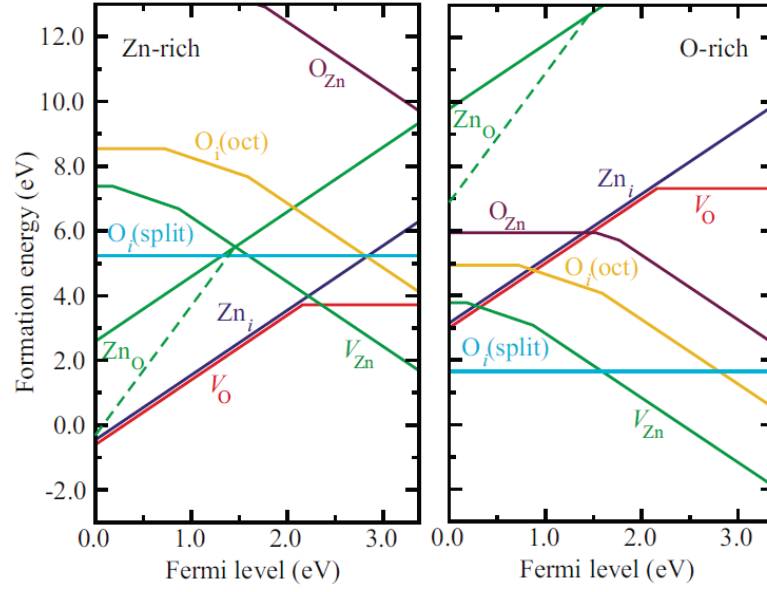


Figure 2.1. Formation energies of intrinsic point defects in ZnO materials grown under Zn-rich and O-rich conditions (adapted from), where the results were attained via the first-principles calculations using density functional theory (DFT) (adapted from [17]).

investigated by performing the first-principles calculations. Defect formation energies are important in understanding the electronic property of ZnO; at equilibrium, the defect concentration can be quantitatively expressed as:

$$c = N_{\text{sites}} \exp\left(-\frac{E^f}{kT}\right), \quad (2.1)$$

where N_{sites} is the number of sites in the lattice, E^f is the defect formation energy, k is Boltzmann's constant and T is the temperature.

2.1.1.1 Oxygen vacancies

Native defect levels in ZnO have been calculated using the hybrid quantum mechanical/molecular mechanical (QM/MM) method, as shown in Figure 2.2.

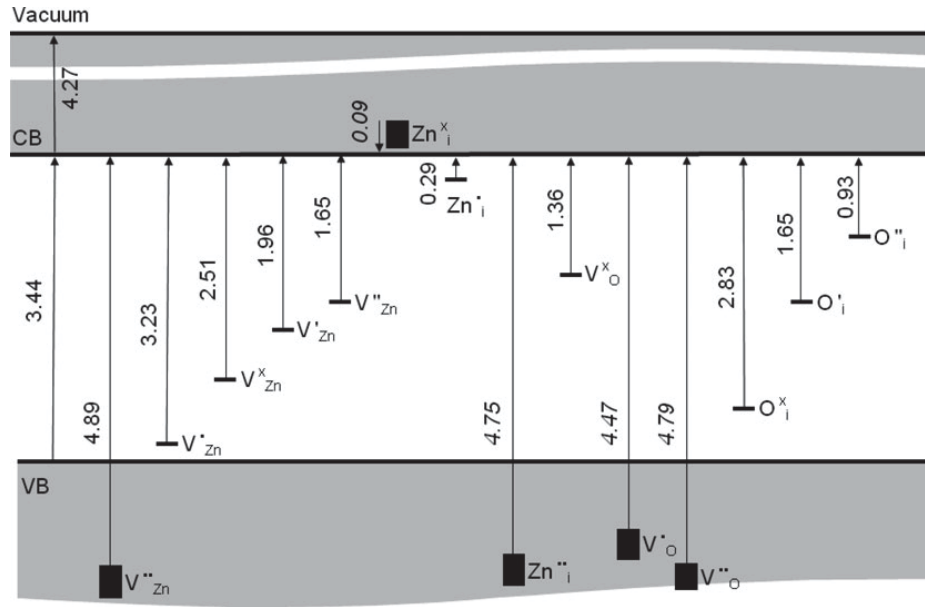


Figure 2.2. Calculated defect energy levels in ZnO using the hybrid quantum mechanical/molecular mechanical (QM/MM) method (adapted from [18]).

Among the donor-like point defects, oxygen vacancies have the lowest formation energy [19] and the presence of oxygen vacancies is a prevalent phenomenon in ZnO materials grown under oxygen deficient conditions [20]. Oxygen vacancies can exist in ZnO in three differently charged forms: namely, neutral charge state, V_O ; single charge state, V_O^+ ; and double charge state, V_O^{++} . Although earlier research reported that V_O is a shallow donor in ZnO [21], recent investigations based on first-principles calculations reveal that V_O^{++} has lower formation energies than V_O and is more easily formed in intentionally *p*-type doped ZnO compensating the acceptors; while for the *n*-type ZnO, V_O can hardly be the main candidate of shallow donors [17]. However, when it comes to nanostructures, oxygen vacancies can be readily formed in ZnO nanowires if the growth takes place in a Zn-rich environment [22].

2.1.1.2 Zinc interstitials

Similar to oxygen vacancy defects, zinc interstitials also behave as donors in ZnO, but their formation energies are slightly higher than oxygen vacancies under both Zn-rich and O-rich conditions, as shown in Figure 2.1. Neutral zinc interstitials in ZnO have a formation energy as high as 6 eV, even under Zn-rich growth conditions. The commonly applied method to create zinc interstitials is to anneal ZnO crystals in Zn vapour and then implement a rapid quenching process [23]. It is noteworthy that the Zn interstitial in its double charge state (Zn_i^{++}) decreases as the Fermi level shifts away from the conduction band and is likely to be a compensating source to the ZnO *p*-type doping [17].

2.1.1.3 Zinc vacancies

There is general agreement that zinc vacancies in ZnO behave as acceptors. McCluskey and Jokela [24] pointed out that zinc vacancies are double acceptors in ZnO with 0/1– being the intermediate acceptor level 0.1 — 0.2 eV above the valence band maximum. Recently, Fabbri *et al.* [25] reported that zinc vacancies are responsible for the green luminescence from the non-polar facets of ZnO nanostructure by comparing monochromatic CL images and the results obtained from *ab initio* calculations. The formation of zinc vacancies is favoured in a O-rich growth environment [22], so they cannot be a prevailing type of defects in the ZnO nanowires grown under a Zn-rich atmosphere. Interestingly, as displayed in Figure 2.2, zinc vacancies exist in five forms in the bandgap: $\text{V}_{\text{Zn}}^{++}$, V_{Zn}^{+} , V_{Zn} , V_{Zn}^{-} and $\text{V}_{\text{Zn}}^{2-}$, indicating that both donor and acceptor dopants have the potential to dwell at the zinc vacancy sites.

2.1.2 Extended defects

An extended defect is a general term referring to structural defects occurring in relatively large scales in ZnO, including grain boundaries, basal stacking faults and lattice dislocations [24]. Extended defects in ZnO may induce three types of light emission: the bound exciton (*Y* line) [26], the electron to defect transition (free-to bound) [27] and the donor-acceptor pair recombination [28]. An emission at 3.31 eV, denoted as *A* line because of its acceptor-like behaviour, was widely observed in various ZnO materials with crystalline deficiencies [29], suggesting that the extended defects could show acceptor behaviour and contribute to the *A* line emission. *A* line has been ascribed to free-to-bound (e, A) transitions in the ZnO samples without intended doping [30], while its behaving mechanism in the *n*-type doped ZnO is still unclear.

2.1.3 Impurities

Due to the use of alkali solutions in the hydrothermal growth of ZnO single crystals, group-I elements (Li, Na and K) commonly exist in the material as inadvertently incorporated impurities [31]. These elements share some common properties: they behave as donors at the interstitial sites [32], while act as acceptors at the substitutional sites replacing Zn [33]. A recent research reveals that Li at the Zn site (Li_{Zn}) is a deep acceptor contributing to the yellow luminescence at 2.2 eV, but Li-related defect complex may induce an acceptor state 150 meV above the valence band maximum [32]. Dingle [34] proposed that Cu^{2+} impurities in ZnO could induce green luminescence due to the transition from Cu to the perturbed ZnO valence-band states. However, for undoped ZnO, the concentrations of impurities are normally low and can hardly be the main cause of deep-level emissions. In recent decades researchers started to focus more

on the effects of intrinsic point defects when investigating the broad green luminescence in ZnO [35].

2.2 Donors and acceptors in ZnO

Table 2.1. Ionisation energies of donors and acceptors in ZnO

Dopant type	Element		Ionisation energy (meV)	Doping method	Reference
<i>n</i> -type dopants	H (I ₄)		46.1	H ₂ annealing; H ₂ plasma	[36]
	Group-III	Al (I ₆)	51.55	CVD with Al powder; wet chemical	[37]
		Ga (I ₈)	54.6	Ga ₂ O ₃ powder	[38]
		In (I ₉)	63.2	In ₂ O ₃ powder	[39]
<i>p</i> -type dopants	Group-I	Li	800 [32]	metalorganic room temperature stirring	[32]
		Na	280 [40]	CVD with NaCl source	[40, 41]
		K	320 [42]	wet chemical	[43, 44]
	Group-V	N	165 [45]	CVD with <i>in-situ</i> N ₂ O or NH ₃ ; nitrogen ion implantation; nitrogen plasma	[45, 46]
		P	620 [47]	CVD with P ₂ O ₅ powder	[47, 48]
		As	130 [49]	Post-annealing ZnO nanowires grown on GaAs substrate	[49, 50]

Donors and acceptors confirmed so far are listed in Table 2.1. Among acceptor candidates for ZnO, although group-I elements, Li, Na and K, behave as acceptors when being incorporated at Zn vacancy sites, interstitial Li, Na and K have been proved to act as donors [24]. Group-V elements — P and As, also found to be acceptors when incorporated substitutionally at the oxygen sites due to their outer shell electron configurations, but their atomic sizes are much larger than oxygen, which may hinder their incorporation into ZnO wurtzite lattice with a proper formation of chemical bonds to the host elements. Nitrogen is considered to be the optimal choice due to its similar atomic size to oxygen and low ionisation energy [51]. However, reliable *p*-conductivity in ZnO has not been achieved either because of the low nitrogen solubility or the formation of compensating defects [52]. Nevertheless, a shallow acceptor level has been reported in N-doped ZnO bulk and nanostructures [45, 53]. On the basis of a donor-acceptor pair (DAP) recombination at ~ 3.24 eV, the binding energy of the acceptor level was determined to be 170 ± 40 meV [45]. Recent extensive theoretical work, however, shows that N substituting O (N_O) leads to a deep acceptor level of 1.3 eV [54] or 1.6 eV above the valence band [55]. These discrepancies between the reported experimental and theoretical values raise questions about the exact chemical nature of the acceptor in N-doped ZnO.

2.3 Bound excitons

Table 2.2 listed the commonly observed I lines in ZnO and their localisation energies. The bound exciton localisation energy is determined by using the transversal free A-exciton (A_T) as the reference [56]. For ZnO, I lines refer to the sharp, narrow peaks observed in the high-resolution near-band-edge (NBE) luminescence spectra at low temperatures [57]. I lines arise from the excitons bound to particular shallow donors in

ZnO and their peak intensities indicate the concentrations of corresponding donors in ZnO, thus I line is a reliable indicator for determining donor impurities in ZnO. Among the identified I line elements — H, Al, Ga and In, hydrogen (I₄ line) is a commonly observed donor element which can be easily incorporated into ZnO during the sample synthesis due to its small size and the ease to form chemical bonds with the host lattice.

Table 2.2. Exciton energies of common I lines in ZnO and their corresponding binding energies (adapted from [56])

Line	Exciton energy (eV)	Localisation energy (meV)	Donor binding energy (meV)	Impurity
I ₀	3.3725	3.4		
I ₁	3.3718	4.1		
I ₄	3.3628	13.1	46.1	H
I ₆	3.3608	15.1	51.6	Al
I ₈	3.3598	16.1	54.6	Ga
I ₉	3.3567	19.2	63.2	In

Nitrogen and hydrogen are important impurities in ZnO because of their already known signature acceptor and donor properties. The following sections present the current status of investigation on nitrogen and hydrogen in ZnO.

2.4 Nitrogen dopants in ZnO

As a promising candidate for *p*-type doping, nitrogen in ZnO has been extensively studied by many workers. A number of optical signatures have been attributed to nitrogen acceptors, such as acceptor bound exciton (A⁰X) and donor-acceptor-pair

(DAP) recombination. Thonke *et al.* [58] observed a peak at 3.22 eV in the PL spectrum of ZnO substrate grown via the seeded chemical vapour transport (SCVT) method. However, there were also contradictory interpretations over the chemical origin of the nitrogen acceptor, predicting via theoretical calculations N_O being a deep acceptor in ZnO with an ionisation energy of 1.3 eV or 0.4 eV, and these energy levels can hardly lead to *p*-type conductivity [54, 59].

Several chemical states of N-related defects are electronically active in ZnO, acting as both donors and acceptors. Isolated nitrogen at O sites was initially detected by ESR and attributed to the shallow acceptor in ZnO [53], whereas it has been established that N_2 on an oxygen site $(N_2)_O$ acts as a shallow donor, which compensates the *p*-type doping [60]. For incorporating acceptors accommodated at the oxygen vacancy sites, singly ionised nitrogen could be chosen as the dopant which generates a donor-to-acceptor pair (DAP) emission with zero-phonon-line position lying in the range from 3.21 to 3.27 eV [61-63].

However, the nature of the N-related acceptor state is complex and has until now remained unclear experimentally and controversial theoretically. The $V_{Zn}-N_O-H^+$ complex were reported as a shallow acceptor and can contribute to the *p*-type conductivity in ZnO [64], while previously it was believed that hydrogen donors may compensate the *p*-type doping in ZnO rather than form acceptor complexes. Based on the combination of density functional calculations and absorption energies of N atoms on ZnO surfaces, Liu *et al.* [65] proposed that the defect complex N_O-V_{Zn} is a shallow acceptor. This complex is preferentially formed on the Zn-terminated surface during ZnO growth but the transition of $N_{Zn}-V_O$ to N_O-V_{Zn} must overcome a large energy barrier of 1.1 eV. More recently, it has been predicted that the N_2 molecule could be

accommodated at the Zn site [66]. By comparing first-principles calculation results and the ESR spectra of N-doped ZnO, Lambrecht and Boonchun [66] concluded that $(N_2)_{Zn}$ is the shallow double acceptor responsible for the DAP transition.

2.5 Hydrogen in ZnO

As shown in Figure 2.3, hydrogen is an amphoteric dopant in most of the listed semiconductors, always counteracting the dominant conductivity of the material. For instance, in the intensively studied wide bandgap semiconductor, GaN, hydrogen will be incorporated as H^+ (losing one electron) if the host is *p*-type; or H^- (gaining one electron) if it resides in the *n*-type material. Due to its amphoteric role in GaN, hydrogen can enhance the solubility of Mg acceptors thus leading to a stable *p*-type conductivity after its thermal out-diffusion. However, because its Fermi level lies above the

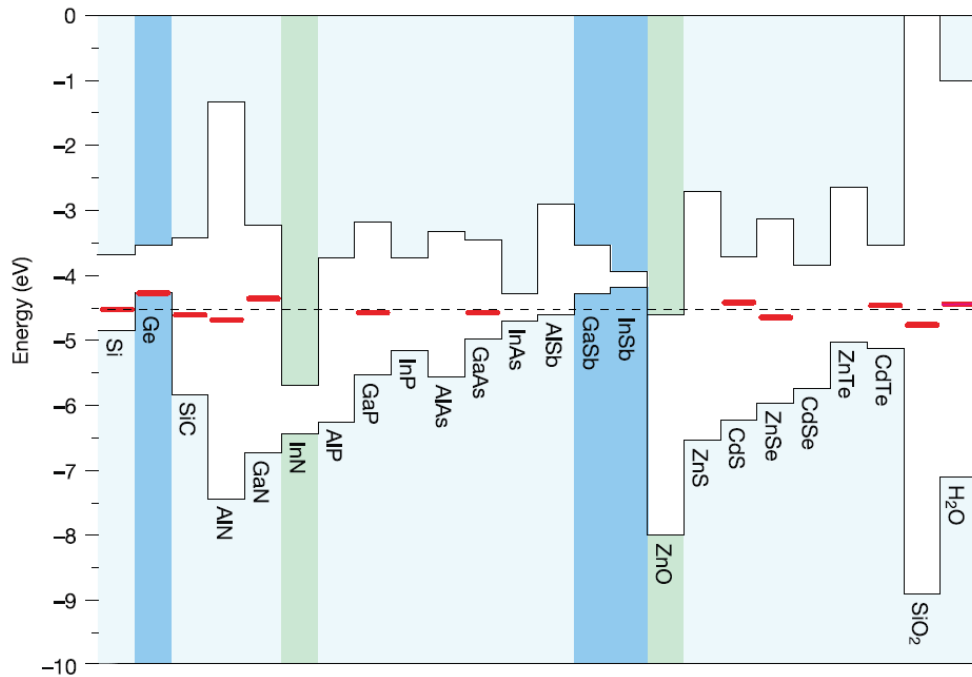


Figure 2.3. Energy band positions of the Fermi level in a series of semiconductors (adapted from [67]). In ZnO, energies of H^0 and H^- are always higher than H^+ , implying that hydrogen is always a shallow donor in ZnO.

conduction band minimum (CBM), hydrogen always behaves as a donor in ZnO passivating the green luminescence and enhancing the near-band-edge emission, which provides an approach of increasing n -type carriers in ZnO [36]. In the meantime, the prevalence of hydrogen donors in ZnO creates a new barrier to producing reliable p -type material [68].

Chapter 3 Experimental Methods

3.1 Substrates and furnace for the sample preparation

3.1.1 Preparation of substrates

3.1.1.1 Substrates for ZnO nanowire growth

Silicon with the orientations of (100) and (111), as well as *a*-plane sapphire, were used as the substrates. Zn atoms in the *c*-plane of ZnO wurtzite lattice align with the O atoms of the *a*-plane sapphire structure [69], so the ZnO nanowires grow vertically on the *a*-plane sapphire substrate.

Silicon wafers were purchased from University Wafer Inc.. Sapphire substrates were bought from MTI Corporation and are polished on both sides. Silicon wafers are firstly cut into 5 mm × 5 mm square pieces with the diamond pen, then ultrasonicated in acetone, isopropanol and MilliQ water successively and blow-dried using N₂ gas.

3.1.1.2 Au catalyst deposition on substrates

Au catalyst can be deposited on the cleaned substrate either by coating the substrate with Au layer on the DYNAVAC SC150 sputter coater, or by depositing colloidal Au nanoparticles onto the substrate via dropcasting. Figure 3.1 shows the DYNAVAC SC150 sputter coater, which is maintained at a current of 100 mA during the Au thin film deposition. A Au layer of ~6 nm thick will be deposited on silicon or sapphire substrate surface after the sputter ion source is turned on for 30 s.



Figure 3.1. DYNAVAC SC150 sputter coater used for Au layer deposition. A Au film with a thickness of ~ 6 nm can be deposited on the substrate by applying the sputter ion source at 100 mA for 30 s.

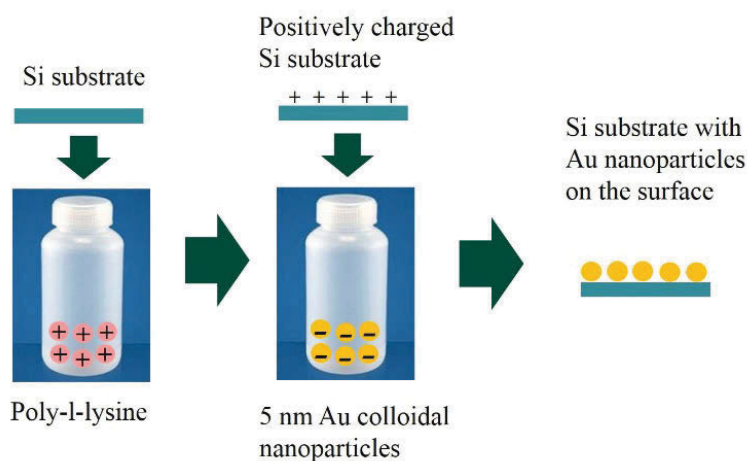


Figure 3.2. Schematic of depositing Au nanoparticles on Si substrate using the electrostatic assembly method. 5 nm Au nanoparticles carrying negative charges adhere to the positively charged Si substrate.

Figure 3.2 displays the procedures of depositing 5 nm Au nanoparticles on the Si substrate. Poly-L-lysine is an L-lysine polymer with a molecular formula of $(C_6H_{12}N_2O)_n$, which possesses a positively charged hydrophilic amino group in water.

By submerging the Si substrate in poly-L-lysine, the surface of the Si substrates becomes positively charged. Then the positively charged Si substrates are immersed in Au colloidal suspension with different concentrations. The Au nanoparticles used in this research were purchased from Cytodiagnostics Inc. biotechnology company, Canada. The as-purchased Au nanoparticles are suspended in alkylthiol organic solvent and are negatively charged, so they will stick on the positively charged Si substrate. The Au nanoparticles in the colloidal suspension are sucked into a piston-driven air-displacement pipette and then dropcast onto the substrate. The substrate with dispersed Au nanoparticles is blown dry using N₂ gas at a low flow rate so that the particles can be evenly distributed on the surface [70]. The residual poly-L-lysine will decompose at temperatures above 250°C, much lower than the ZnO nanowire growth temperature, so the effect of residual organic solvent can be excluded.

3.1.1.3 ZnO single crystal for hydrogen doping

The *a*-plane ZnO single crystal used for hydrogen plasma treatment was purchased from MTI Corporation, USA. The bulk ZnO samples were grown using the hydrothermal method with a purity greater than 99.99% by weight ratio. Minute amount of impurities, including Mg (<0.0005%), Al (<.0030%), Si (<0.0030%), Ti (<0.0010%), Cu (<0.0030%), Fe (<0.005%), and Ca (<0.0005%), are also present in the sample. The single crystal sample is 0.5 mm in thickness with both sides polished to a surface roughness of ~1 nm. The purchased ZnO crystal was cut into 5 mm× 2.5 mm rectangle sections and ultrasonically cleaned following the aforementioned substrate preparation procedures.

3.1.2 Construction of the gas-controlled furnace

A one-chamber horizontal furnace was used for growing ZnO nanowires. The temperature of the furnace is controlled by the EURO THERMO 3200 PID temperature controller with a type K thermocouple sensor in the centre detecting the heat. The gases were regulated by the gas controllers with the setpoint accuracy to 1 sccm for Ar and 0.1 sccm for O₂. During the ZnO nanowire growth, the source material and the substrate were placed at appropriate locations within the heating zone, as shown in Figure 3.3(a). Two pumps were used in this project, as listed in Table 3.1. EDWARDS 8 rotary vane

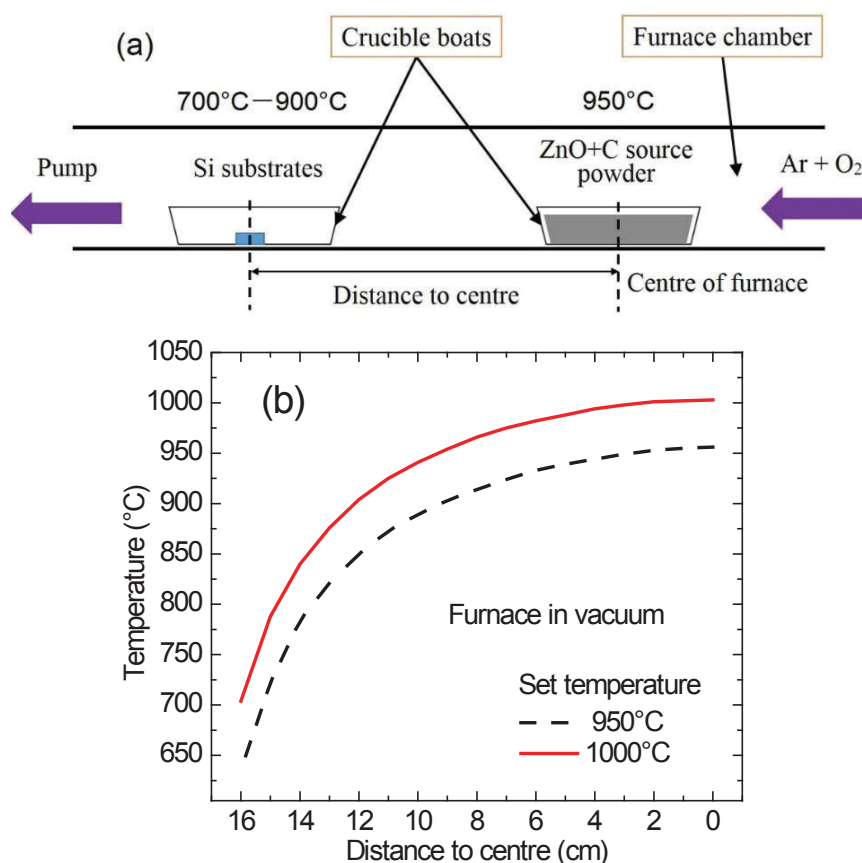


Figure 3.3. Nanowire growth setup in the furnace and the temperature profile with the centre of the chamber set to be 950°C (black dashed curve) and 1000°C (red solid curve), respectively. (a) details the boat alignment and gas flow orientation in the furnace. (b) shows the temperature decrease with the measuring point moving further away from the centre.

pump can pump the chamber to a higher vacuum level than the EDWARDS XDS 10 scroll pump. For both pumps, pumping rates were too high. Different valve configurations were designed and tested so that the original pumping rate could be controlled manually with the range from 7.5×10^{-4} to 2 Torr. The pressure in the tube could be kept constant in the range of 0.1 — 1 Torr by adjusting the valve.

Table 3.1. Pumps used in the nanowire growth

Pump model	Ultimate vacuum
EDWARDS XDS 10	5.3×10^{-2} Torr
EDWARDS 8	7.5×10^{-4} Torr

3.1.3 Growth of ZnO nanowires by carbothermal reaction

ZnO is a thermally stable oxide material with a melting point of 1975°C, which is higher than the maximum temperature on the furnace (1100°C). Although ZnO can decompose into Zn vapour and O₂ gas at a relatively low temperature (~1000°C) when using a low ambient pressure: $2\text{ZnO} \Rightarrow 2\text{Zn} \uparrow + \text{O}_2 \uparrow$ [71], the Zn vapour that can be generated by the decomposition of ZnO powder is insufficient as a Zn source for the nanowire growth. An adequate Zn vapour supply can be obtained via the carbothermal reduction by heating the ZnO and graphite powder mixture [72]:



The generated Zn vapour is then transported to the location of the substrate in the tube

furnace by Ar carrier gas. The Zn vapour precipitates at the melted Au droplets and reacts with the oxygen gas producing ZnO:



3.2 Doping by plasma annealing

The plasma used for implanting ZnO nanowires with nitrogen was generated in a vacuum chamber and the ion flow intensity is adjusted via the AG 0201HV-OS high voltage rf plasma power controller, as presented in Figure 3.4 with a photo of the plasma chamber shown in (a) and the drawn schematic shown in (b). The column chamber is equipped with a rf plasma source, which ionises the gas introduced into the chamber via the gas pipe connected to the gas cylinder. By adjusting the forward and reverse power settings, plasma sources of different strength levels can be obtained. This device achieves optimal performance when the radio frequency is set to be 160 kHz. A relatively high gas ionisation rate can be achieved using a voltage of around

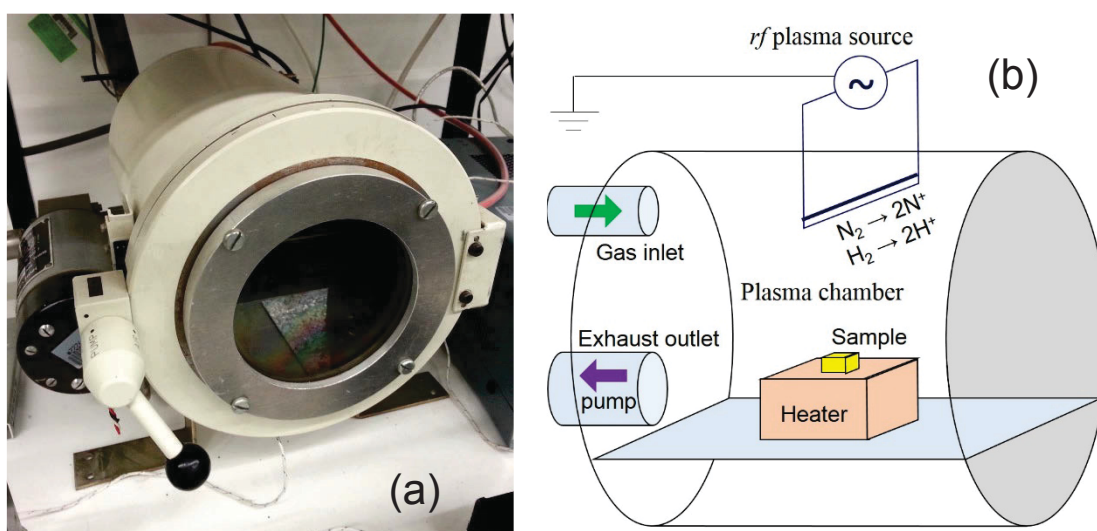


Figure 3.4. Diagrams of the rf plasma chamber. A picture taken on the plasma generator is shown in (a), and the functioning mechanism of this instrument is illustrated in (b).

200 V, which is much lower than the voltage used for DC ion implantation, so the damage on the crystal lattice structure is highly reduced and confined to the top few nanometres on sample surface.

The heater in the chamber is used as a sample holder during the plasma treatment. By heating the ZnO samples to high temperatures, the uniform dopant incorporation into the crystal lattice is effectively facilitated. A thermometer connecting to the heater measures the temperature of the samples on the holder and the value is displayed on the same panel with the set heating temperature. For doping ZnO nanowires with nitrogen, 5 sccm constant N₂ gas is introduced into the plasma chamber. The nanowires are heated to 300°C before the plasma source is turned on. The plasma power and voltage are 20 W and 230 V with the duration varying from 30 to 150 min. For doping bulk ZnO with hydrogen, one *a*-plane single crystal sample was heated to 200°C under a constant hydrogen gas flow of 10 sccm. As the temperature reaches 200°C, the rf plasma, with the power and voltage set to be 15 W and 187 V, is turned on for 120 s.

3.3 Characterisation techniques

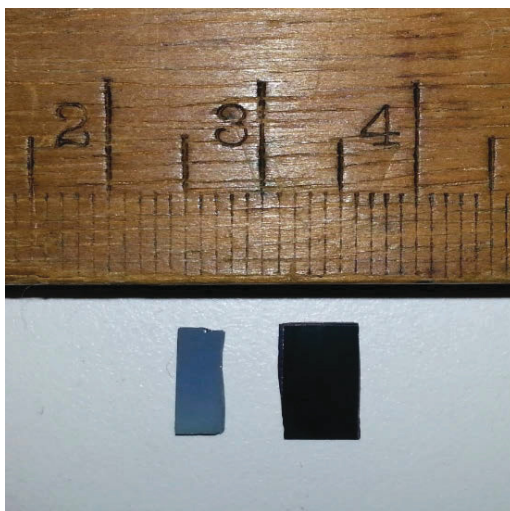


Figure 3.5. Optical photograph of two ZnO nanowire samples used in this study.

Figure 3.5 displays the photo of two typical ZnO nanowire samples. The samples for post-growth treatments and characterisation have dimensions of $0.3 - 0.5 \times 0.8 \text{ cm}^2$. The two samples appear differently in surface colour and luster, which is largely due to the size discrepancy of the grown nanowires. The light propagates differently in ZnO nanowires with different geometrical properties. The left sample is covered with thin nanowires; while the right sample is comprised of nanowires with larger diameters.

3.3.1 Morphological and structural analysis

Zeiss SUPRA VP 55 field-emission scanning electron microscope (FESEM) was used for performing the morphological measurements on the nanostructures. Equipped with the field emission electron source, the electron beam inside the microscope column is more efficient and this FESEM provides a spatial resolution of $\sim 1 \text{ nm}$.

The instrument schematic in Figure 3.6 illustrates the functioning mechanism of the X-ray diffractometry, which serves as an effective approach for determining the crystal orientation and crystallinity of solid materials. For ZnO nanowires, the XRD diffraction pattern can reveal the nanowire alignment as well as their crystal quality. The sample

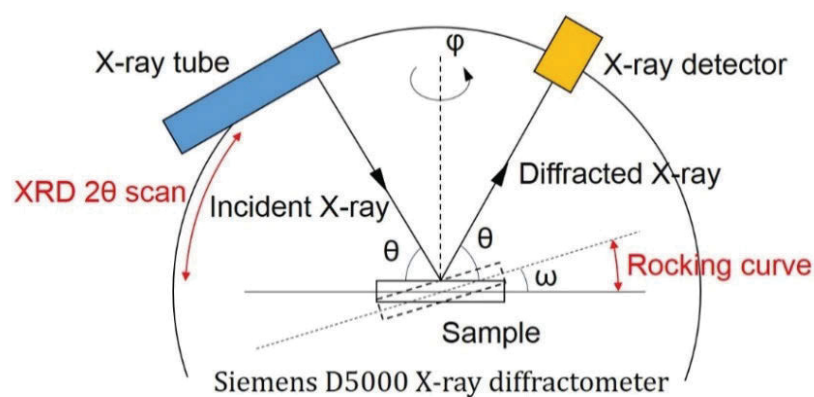


Figure 3.6. Schematic of the X-ray diffractometer. The red arrows denote the 2θ scan and rocking curve measurement modes on this instrument.

is scanned by rotating the X-ray from an angle of 0 degree to an angle of 90 degrees obeying Bragg's Law [73]:

$$n\lambda = 2d\sin\theta. \quad (3.4)$$

When the path difference equals n wavelengths, constructive interference occurs. By rotating the arm along the ω angle, the X-ray rocking curve is collected, which indicates the mosaic spread and the inhomogeneity of the sample surface.

Raman measurements were performed using a LabRAM HR800 spectrometer (Horiba Jobin Yvon) with a 458 nm excitation laser tuned to 1 mW. The Raman spectra were collected in backscattering geometry with a spectral resolution of 0.3 cm^{-1} .

3.3.2 Cathodoluminescence (CL)

Cathodoluminescence is the luminescence from the sample induced by the electron beam excitation. The high energy electron beam excites electrons in the valence band to the conduction band, leaving a hole in the valence band. Radiative recombination between the electron and the hole can emit light via a number of possible channels as

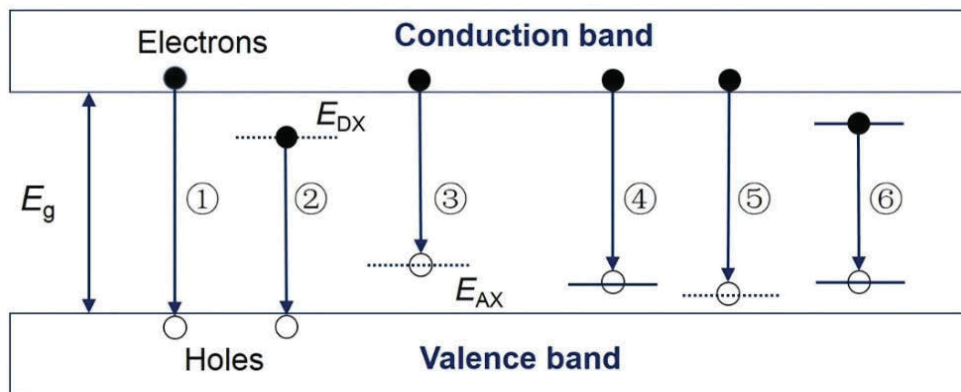


Figure 3.7. Radiative near-band-edge transitions in ZnO bandgap. The transitions with different energies correspond to the presence of intrinsic defects or incorporated dopants.

shown in Figure 3.7. This diagram introduces the typical radiative channels in the wide bandgap semiconductor material. The luminescence radiations corresponding to different energy levels inside the bandgap are listed as follows:

- 1) Free exciton (FX) [74]:

$$E_{\text{FX}} = E_g - E_X. \quad (3.5)$$

Here, E_g is the bandgap energy, E_X is the binding energy of the free exciton.

- 2) Neutral donor bound exciton (D^0X) [74]:

$$E_{D^0X} = E_g - E_X - E_D, \quad (3.6)$$

where E_D represents the dissociation energy of the exciton bound to neutral donors.

- 3) Neutral acceptor bound exciton (A^0X) [74]:

$$E_{A^0X} = E_g - E_X - E_A, \quad (3.7)$$

where E_A is the binding energy of the exciton bound to neutral acceptors.

- 4) Free electron to acceptor transition (e, A) [75]:

$$E_{\text{FA}} = E_g - E_A + \frac{k_B T}{2}, \quad (3.8)$$

where k_B is the Boltzmann constant and T is the temperature of the system.

- 5) Free-to-bound transition (e, B) [30]:

$$E_{\text{FB}}(T) = E_g(T) - E_a + k_B T, \quad (3.9)$$

where E_a denotes the energy level of the acceptor.

6) Donor-acceptor-pair (DAP) recombination [76]:

$$E(r) = E_g - (E_D + E_A) + \frac{e^2}{\epsilon r}. \quad (3.10)$$

Here, e is the electric charge, ϵ is the dielectric constant and r represents the distance between the donor and the acceptor involved in this type of transition.

In recent decades, with the emerging and prosperity of nanotechnology and low dimensional quantum devices, CL has gained increased attention from the researchers due to its high energy range for analysis of wide bandgap materials and the capability of performing spatially resolvable optical measurements.

3.3.2.1 CL experimental setup

CL measurements were carried out on the FEI Quanta 200 SEM with an aluminium parabolic CL mirror attached to microscope chamber. With a high energy electron beam applied to the sample surface, the luminescence is emitted from the sample and collected by the CL mirror and directed to an optical fibre, which is connected to either the OceanOptics QE6500 digital spectrometer or the optics to the Oriel MS257 1/4 m monochromator. The monochromator disperses the light to a certain wavelength range and the dispersed light is projected onto a Hamamatsu S7011-1007 charge coupled device (CCD) sensor, which is attached to the lateral port of the monochromator, as shown in Figure 3.8. The OceanOptics QE6500 spectrometer covers a luminescence range from 200 nm to 1000 nm, while the Hamamatsu CCD detector provides better CL spectral resolution by letting the light pass through a monochromator with high-resolution echelle gratings.

Four gratings are available on the monochromator system, Grating 1 to Grating 4,

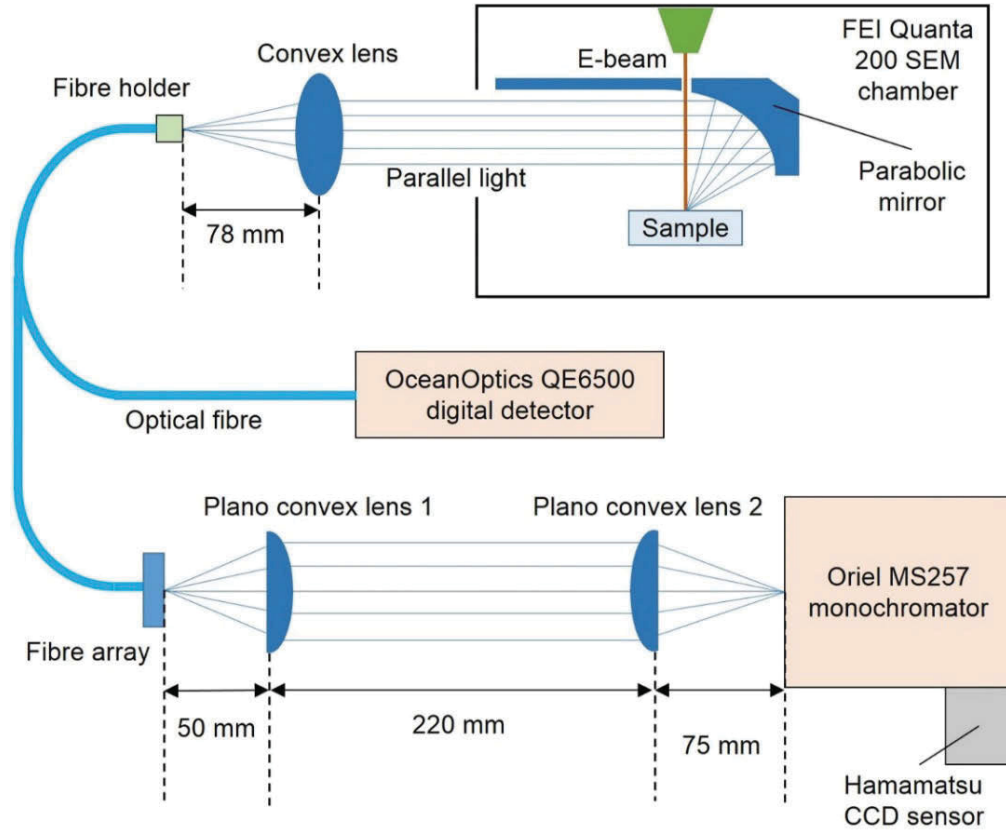


Figure 3.8. Schematic of optics setup on the SEM for CL measurements. The optics are attached to FEI Quanta 200 ESEM with an aluminium parabolic mirror used for collecting the light from the sample.

corresponding to a wavelength range scale of 50 nm to ~ 1000 nm, respectively. For measuring the fine structure of the near-band-edge emission, Grating 1 is normally selected, which can give a spectra with 0.05 nm per pixel. By properly setting the grating and the centre wavelength, CL images at different wavelengths can thus be collected. The spatially resolved CL is collected by a photomultiplier tube (PMT) which is connected to one end of the monochromator.

3.3.2.2 Calibration of wavelength and intensity

The parabolic mirror used for gathering the light from the sample is made of aluminium,

which can absorb light in the UV range [77]. To maintain the accuracy of CL measurements, the system response curve is used to correct all spectra presented in this thesis. The system response curve intensity calibration can be expressed using the following equation:

$$\text{response curve} = \frac{I(\text{standard irradiance})}{I(\text{collected spectrum})} \quad (3.11)$$

Spectrum wavelength on OceanOptics detector was calibrated by the manufacturer. Due to the wide wavelength range on OceanOptics spectrometer (200 — 1000 nm), the effects of the optical absorption need to be taken into consideration while calibrating the as-collected CL spectra. The optics response curve is shown in Figure 3.9 with the calibration formula presented in Equation (3.11). Oriel 63358 Quartz Tungsten Halogen with a wavelength range of 300 — 2400 nm, operating at 45 W, was used as the CL intensity calibration light source.

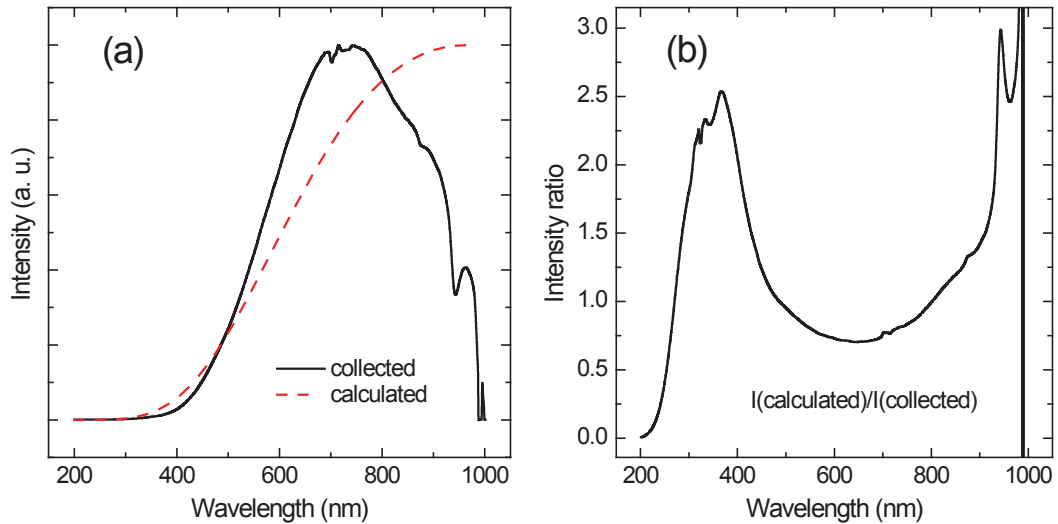


Figure 3.9. System optics response curve for OceanOptics spectrometer. (a) displays the collected spectrum of W halogen light source (black solid curve) and the calculated curve using the standard irradiance equation (red dashed line); (b) shows the response curve by dividing the calculated intensity by the collected spectrum.

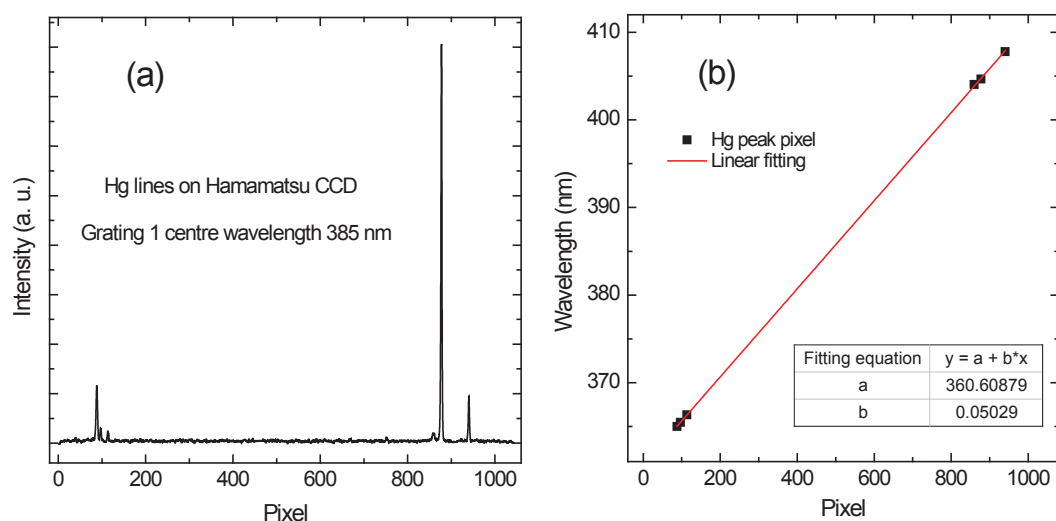


Figure 3.10. Wavelength calibration for the Hamamatsu CCD using Grating 1 on the monochromator with the centre wavelength set as 385 nm. (a) shows the spectrum of the Hg lamp at Grating 1, centre wavelength 385 nm; (b) displays the fitted linear function for converting the unit from pixel to nm for wavelength.

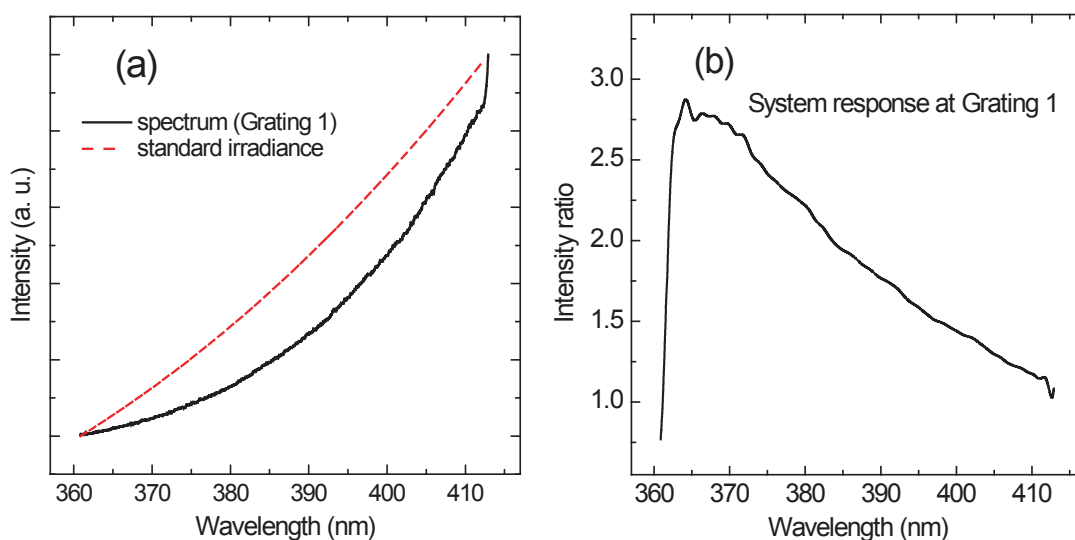


Figure 3.11. System optics response curve for Grating 1 on Oriel monochromator at centre wavelength 385 nm. (a) displays the collected spectrum of W halogen light source (black solid curve) and the calculated curve using the standard irradiance equation (red dashed line); (b) shows the response curve by dividing the calculated intensity by the collected spectrum.

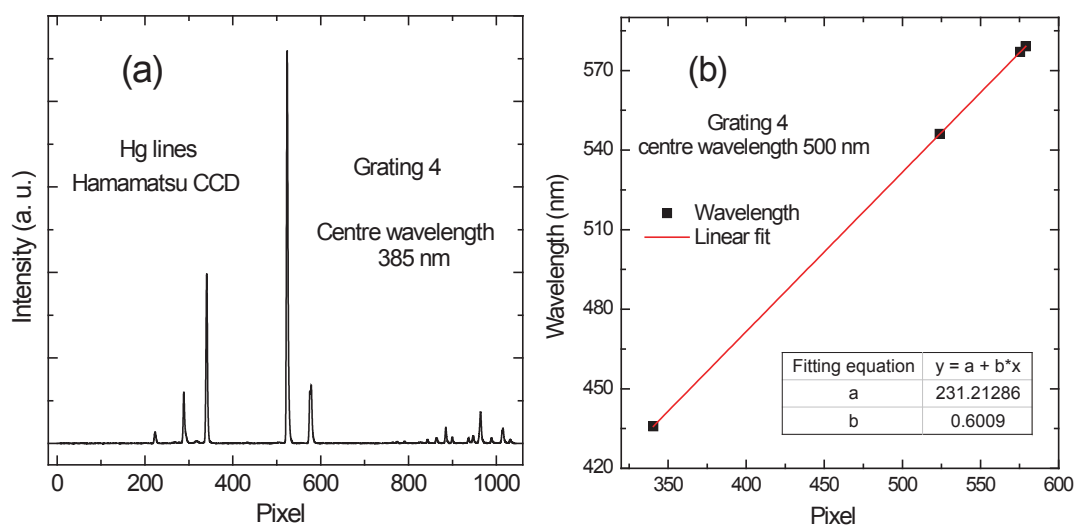


Figure 3.12. Wavelength calibration for the Hamamatsu CCD using Grating 4 on the monochromator with the centre wavelength set as 500 nm. (a) shows the spectrum of the Hg lamp at Grating 4, centre wavelength 500 nm; (b) displays the fitted linear function for converting the unit from pixel to nm for wavelength.

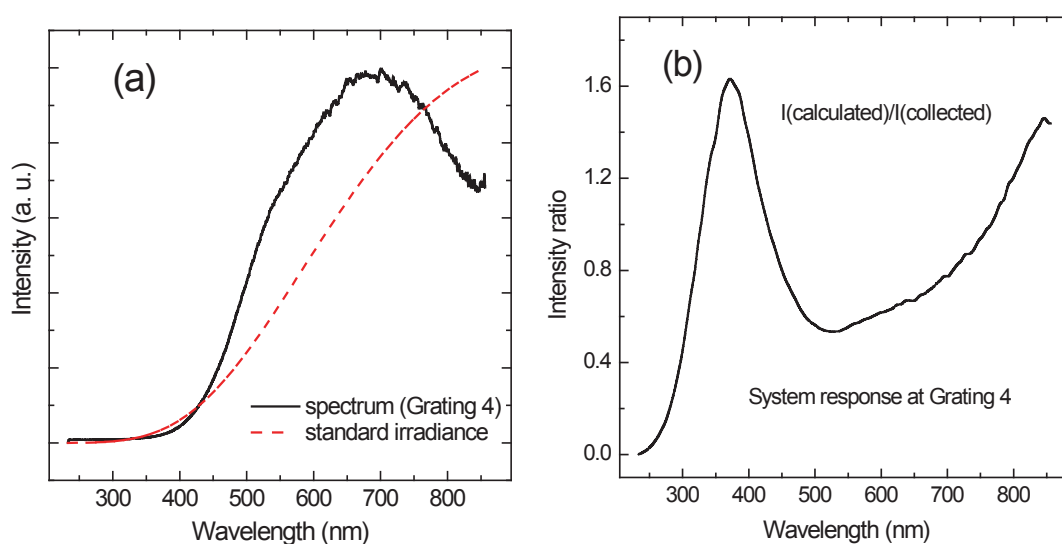


Figure 3.13. System optics response curve for Grating 4 on Oriel monochromator at centre wavelength 500 nm. (a) displays the collected spectrum of W halogen light source (black solid curve) and the calculated curve using the standard irradiance equation (red dashed line); (b) shows the response curve by dividing the calculated intensity by the collected spectrum.

The spectrum collected on the Hamamatsu CCD covers a wavelength range of only 50 nm at Grating 1, as shown in the pixel-to-wavelength calibration in Figure 3.10. There is no significant intensity change over this range, as displayed in Figure 3.11. Consequently, no intensity calibration is needed for processing the data collected using Hamamatsu CCD at Grating 1. This monochromator at Grating 1 mode is suitable for investigating detailed near-band-edge excitonic emissions utilising its capability for high-resolution CL measurements.

When using Grating 4, the spectrum covers a wavelength range of about 620 nm with the Hg lamp feature shown in Figure 3.12. The intensity calibration spectra using the W halogen are displayed in Figure 3.13(a) with the response curve shown in (b).

3.3.2.3 Simulation of the CL generation depth

In nanostructures, the material can exhibit different optical properties with changes in the spatial position; for bulk materials, the sample properties can be regarded as uniform in the xy plane; whilst most samples also possess different properties along the z -axis originating from the inhomogeneities in the depth direction caused by doping or surface oxidation. The 2-dimensional property changes can be investigated at the nanoscale using an SEM with the electron beam scanning across the sample surface in a point-by-point and line-by-line manner. In this research project, depth analysis in the z -direction is achieved by systematically increasing the electron accelerating voltage so that the materials at different depths can be probed and the correlated properties can be investigated.

The CL is generated by electron beam delivering energy to the material and exciting the electrons to the conduction band, so the CL intensity distribution in the sample is

determined by the electron energy loss inside the material [78]. The CL generation depth is correlated to the electron beam maximum energy dissipation depth, which can be expressed as [79]:

$$x_E = \frac{R(1+2\gamma-0.21\gamma^2)}{2(1+\gamma)^2}, \quad (3.12)$$

where the energy range R has the form:

$$R = \frac{2.76 \times 10^{-11} A E_0^{5/3}}{\rho Z_{\text{ZnO}}^{8/9}}. \quad (3.13)$$

Here, parameter $\gamma = 0.187Z^{2/3}$, which involves the electron energy loss due to multiple inelastic collisions. A is the atomic weight, E_0 is the incident electron energy, ρ represents the density of ZnO and the effective atomic number Z for ZnO can be calculated as $Z_{\text{ZnO}} = \sqrt[2.94]{f_{\text{Zn}} \times Z_{\text{Zn}}^{2.94} + f_{\text{O}} \times Z_{\text{O}}^{2.94}} = 27.7337453$, where $Z_{\text{Zn}} = 30$ and $Z_{\text{O}} = 8$ are the atomic numbers of Zn and O, respectively; f_{Zn} and f_{O} are the associated electron number fractions: $f_{\text{Zn}} = 30/38$, $f_{\text{O}} = 8/38$.

The Monte Carlo CASINO program simulates the electron trajectory in solids, both for bulk and thin film systems. This program is widely used for predicting the signals

Table 3.2. Parameters for CASINO CL generation depth simulation

Sample	ZnO substrate
Weight fraction (%)	Zn: 80.3397; O: 19.6603
Electron energies	1 — 30 keV (1 keV per step)
Beam radius	5 nm
Number of electrons	1,000,0000
Minimum electron energy	0.05 keV

observed in SEM measurements [80], such as scattered electrons, X-rays and luminescence. By simulating the electron-material interaction, an energy loss profile inside the sample can be created, which indicates the CL generation depth. The parameters for carrying out the Monte Carlo CASINO simulation are presented in Table 3.2. An electron accelerating voltage in the range of 1 — 30 keV is applied with a step voltage of 1 keV, and the electron beam radius is set to be 5 nm. The energy loss in the material were obtained by simulating 1 million electrons interacting with the bulk ZnO, which possesses a density of 5.61 g/cm³.

Figure 3.14 shows the electron energy loss distribution over the longitudinal section in the semiconductor at electron beam voltages of 1 keV, 5 keV, 10 keV and 30 keV using the CASINO code. The electron-material interaction volume becomes larger with

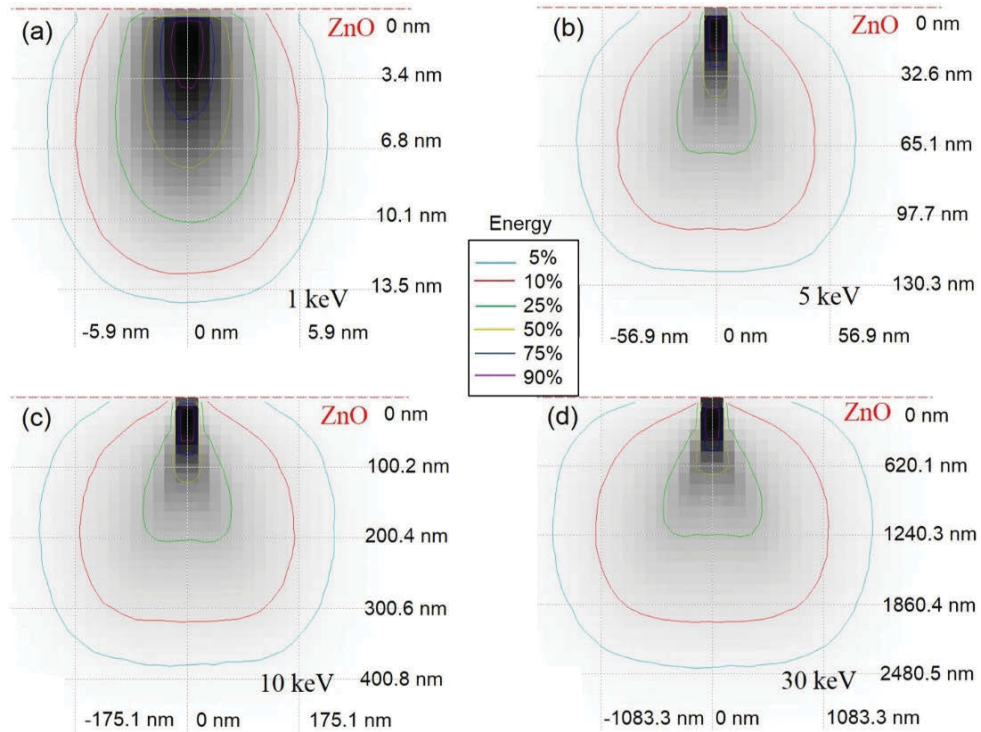


Figure 3.14. Incident electron energy loss profile in ZnO. The major CL generation volume increases slower than the maximum range of the electrons.

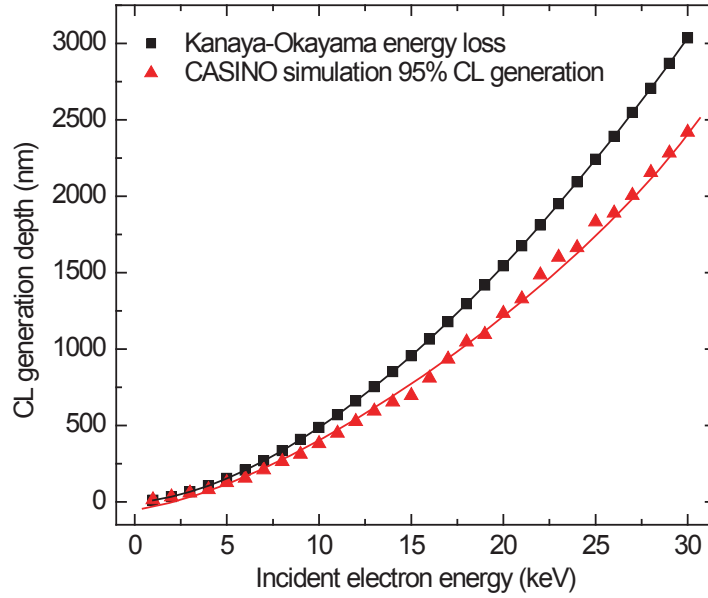


Figure 3.15. CL generation depth as a function of incident electron energy. The CL depth simulated using the CASINO program exhibits similar tendency to the CL energy loss calculated using the Kanaya-Okayama equations.

increasing the incident electron energy. At 1 keV, the CL generation volume is close to the surface of the material; while at higher electron beam voltages, the majority of the CL is generated from the deeper volume of the sample. The CL generation depth versus electron energy obtained using CASINO simulation and the results calculated from the Kanaya-Okayama equation [Equation (3.12)], are plotted in Figure 3.15. The thickness of the material, which contributes to 95% of the CL, increases from 14 nm at 1 keV to ~2450 nm at 30 keV. ZnO nanowires in this research normally have the length of several hundred nanometres, for which the electron beams of 5 kV to 10 kV are appropriate for the measurements. While for the bulk ZnO sample, an electron beam at around 5 kV is optimal for surface effect investigations and higher voltages for bulk properties inside the sample.

3.3.3 X-ray absorption near edge structure (XANES)

XANES measures the absorption of X-rays as a function of X-ray photon energy. Near edge refers to a low photoelectron kinetic energy in the range of 5 — 50 eV. With a low kinetic energy, the excited photoelectron can be backscattered multiple times between neighbouring atoms thus enhancing the photon emission. There are two types of detection modes in XANES spectroscopy: the total fluorescence yield (TFY) that measures the amount of emitted fluorescence photons, and the total electron yield (TEY) that monitors the electrical current produced by the emitted electrons. By probing the angular momentum of the unoccupied electron states in the energy region above the selected atomic core ionisation level, XANES provides information of the electron transitions from the selected core level to the unoccupied states.

The XANES measurements were carried out on the soft X-ray spectroscopy (SXS) beamline at Australian Synchrotron, as illustrated in Figure 3.16. Electromagnetic radiation is generated from the synchrotron storage ring. The light collected on the SXS beamline is modulated into soft X-ray photons with required energies via the

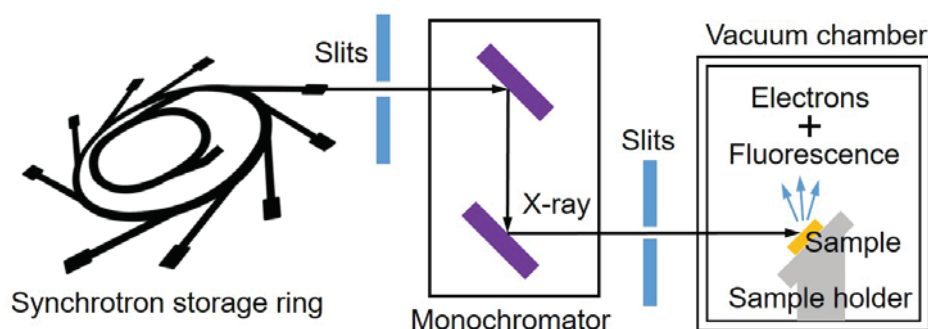


Figure 3.16. Schematic of the apparatus for XANES measurements on the soft X-ray spectroscopy beamline at Australian Synchrotron. X-ray photon energy can be adjusted to continuously vary values via the monochromator, which provides an ideal source for measuring the near-edge X-ray absorption profile.

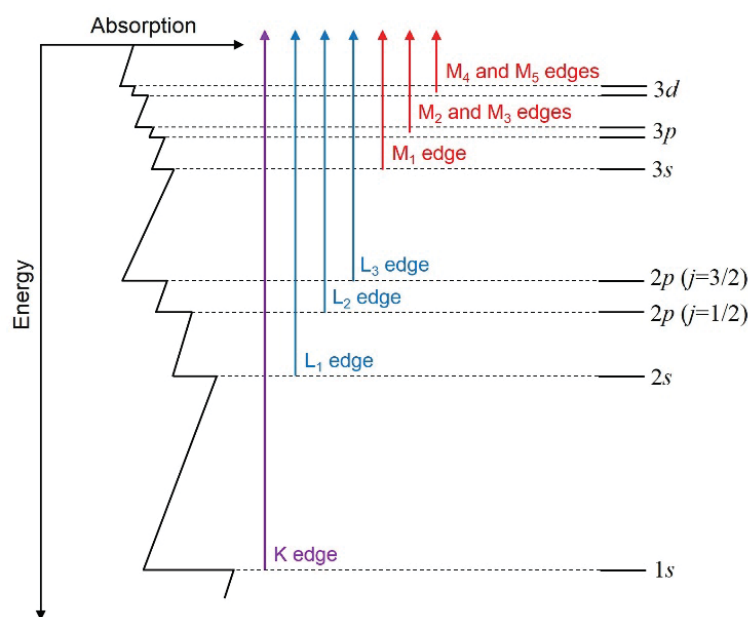


Figure 3.17. X-ray absorption edge electron transitions. *K*-, *L*- and *M*-edges are displayed with the arrows denoting the possible transition channels. The *L* edge is splitted into fine structures by the total angular momentum quantum number j .

monochromator and associated optics. The photons are then guided to the target sample, which is located in a high vacuum chamber. Electrons and fluorescence are emitted from the ZnO samples when hit by the high energy X-ray photons. In XANES spectroscopy, these two types of emissions constitute TEY and TFY spectroscopies, respectively. The SXS beamline provides continuously variable X-ray radiation with the photon energy ranging from 100 to 3000 eV, which is optimal for probing the near-edge structures of elements Zn, O and N.

Figure 3.17 displays the X-ray absorption edge electron transitions, where principal quantum numbers $n = 1, 2$ and 3 , corresponding to the *K*-, *L*- and *M*-edges. For instance, *L*₃-edge electron transitions include the excited 2*p* states with a total angular momentum quantum number $j = 3/2$.

Chapter 4 Au-catalysed growth of ZnO Nanowires

4.1 Introduction

Au is widely used as a catalyst for the growth of various semiconductor materials, such as Si whiskers [81], GaAs nanowires [82] and ZnO nanorods [83]. Figure 4.1 illustrates the ZnO nanowire growth following the VLS and VS mechanisms using Au as the catalyst. In the vapour-liquid-solid (VLS) growth of ZnO nanowires, the Au catalyst

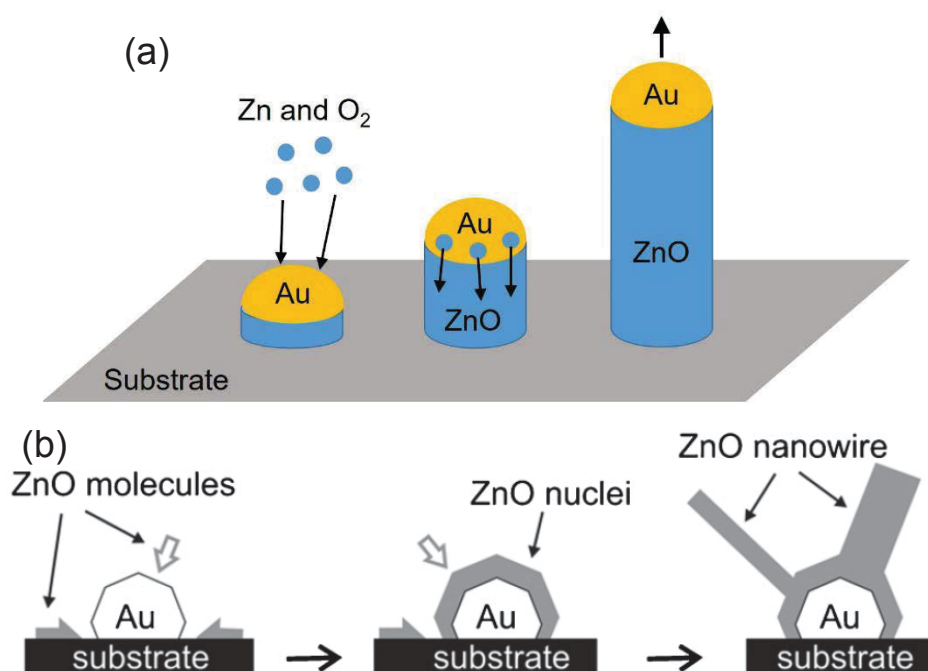


Figure 4.1. Schematic of nanowire growths via the VLS and VS mechanisms. (a) The Au catalyst dot stays at the tip area of the nanowire during the VLS nanowire growth. The source vapour is deposited on the Au droplet and diffused into the main structure. (b) Zn vapour precipitates on the Au site and grow on top of the Au droplet (adapted from [84]).

adsorbs Zn vapour to a supersaturation level and the CVD process takes place beneath the Au nanoparticle catalyst, which remains at the tip of nanowires. Whereas in the vapour-solid (VS) growth the Au nanoparticle seeds act as nucleation sites for ZnO deposition and remain on the substrate [85]. Prior to the growth, a nucleation layer was formed on the interface between the substrate and the grown structure, so ZnO nanorods can grow from the interfacial layer and the lattice mismatch has limited effect on the nanorod vertical alignment.

In this thesis, Au films and colloidal Au nanoparticles are used as catalyst to initiate the ZnO nanowire growth. Although catalyst-free ZnO nanowire growth was previously reported using the MOCVD technique by other workers [86], the use of Au has advantages. In the VLS growth, diameters of semiconductor nanowires can be effectively controlled by changing the size of the Au particles guiding the growth [87]. In the VS growth, Au can form an intermediate layer when heated to about 700°C, reducing the effects of the lattice mismatch on the growth of ZnO nanowires, which is essential for the production of low-cost, high-quality nanowires [88]. This chapter demonstrates the effects of Au catalyst morphology, growth temperature and carrier gases on the growth of ZnO nanowires.

A major effort in this project has involved the optimisation of ZnO nanowire growth including the deposition of catalytic Au film or Au nanoparticles, ratio of ZnO powder and graphite used in the source material, temperatures of the source and substrate, reactor pressure, and flow rates of carrier gases. Some representative results obtained from this growth optimisation are presented below.

4.2 ZnO nanowire growth using Au films

4.2.1 Morphology of catalytic Au islands before nanowire growth

The Au-coated Si substrate was annealed at 700°C, the optimal growth temperature for the well-aligned ZnO nanowires. After annealing the Au-coated Si substrate at 700°C, the Au layer forms droplets covering the substrate surface. The secondary electron (SE) image and the backscattered electron image are shown in Figure 4.2(a) and (b), respectively. The Au droplets in Figure 4.2 show a wide distribution of sizes, which is unsuitable for the growth of ZnO nanowires with uniform diameters. When growing ZnO nanowires, the Zn vapour was deposited on the Au droplets and then the ZnO nanowires will start to grow after the oxygen is introduced. However, in the whole substrate annealing procedure, neither ZnO and graphite mixed powder was located in

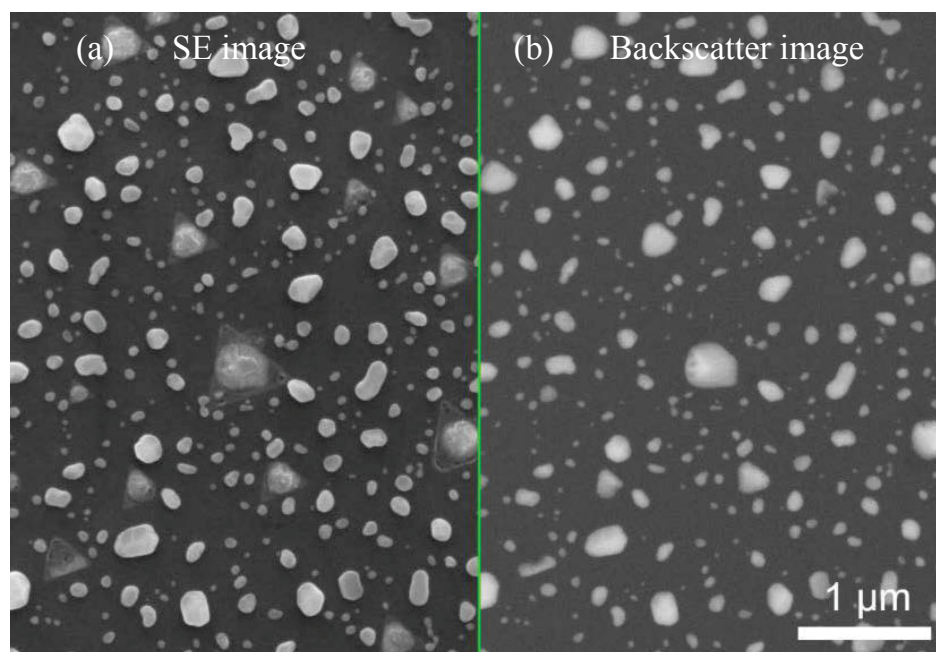


Figure 4.2. Si substrate with 6 nm Au film annealed at 700°C for 30 min. The Au layer becomes droplets covering the substrate surface after annealing. (a) shows the secondary electron (SE) image while the backscattered electron image is displayed in (b).

Table 4.1. Lattice mismatches between ZnO and substrates used in this research

Substrate material	Lattice mismatch with ZnO (%)
Si(111)	40.3 [89]
Si(100)	40.1 [90]
Sapphire(0001)	18.4 [91]
Sapphire(11 $\bar{2}$ 0)	0.08 [92]

the centre of the furnace nor the oxygen gas was introduced into the chamber.

The lattice mismatch between ZnO and Si(100) substrate was reported to be 39% according to Phan *et al.* [93], or 40.1% according to Özgür *et al.* [90]. *A*-plane sapphire (11 $\bar{2}$ 0) has a lattice mismatch of 0.08% with wurtzite ZnO due to their almost overlapped oxygen ions [92], which is an optimal choice for ZnO nanowire growth (Table 4.1). In the nanowire growth, Au catalyst becomes droplets at elevated temperatures, which can mitigate the effect of lattice mismatch. The Au droplets act as nucleation sites and the ZnO nanowires grow directly from the Au dots when the zinc and oxygen source materials are available, so the influence of the lattice mismatch on the growth of ZnO nanowires is significantly reduced. Normally obtained Si wafers possess a native oxide layer, SiO₂. This amorphous SiO₂ layer also hinders the direct contact between the Si and ZnO thus further reducing the influence of the crystal lattice mismatch on the nanowire alignment.

Although intermetallic compound can be formed by heating up Au and Al [94], no obvious reaction between Au layer and sapphire substrate was observed, as shown in Figure 4.3. Hexagonal Au droplets are formed on the sapphire substrate surface after

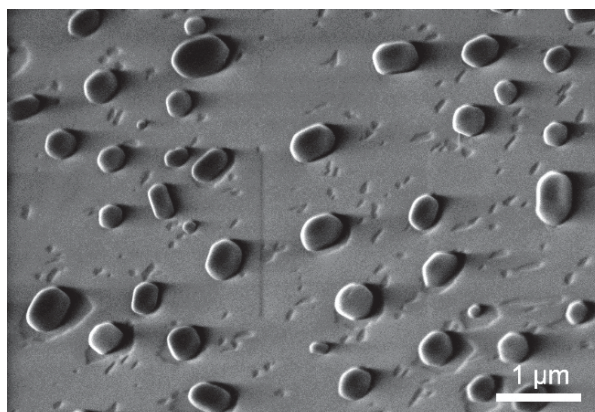


Figure 4.3. Au-coated α -plane sapphire substrate annealed at 700°C for 30 min. The Au layer forms Au dots with diameters of rough 500 nm, showing that Au is less reactive to sapphire even when heated to 700°C.

the annealing in Ar at 700°C for 30 min. This annealing temperature is lower than melting points of both the sapphire substrate (2030°C) and Au (1064°C), indicating that the Au could also form liquid alloy with sapphire at relatively low temperatures. Au dots are more uniform in size and have more homogeneous distribution on the sapphire substrate compared with those on the Si substrate (Figure 4.2), suggesting that the surface strain on the sapphire substrate is more homogeneous than that on the Si substrate [95].

4.2.2 Effects of temperature on ZnO nanowire growth

As shown in Figure 3.3(a), the ZnO and graphite admixture is placed at the centre of the horizontal furnace, which can be heated to 950°C—1000°C in order to generate

Table 4.2. Temperature ranges used in the growth of nanowires

Source temperature (°C)	Substrate temperature (°C)
950 — 1000	700 — 950

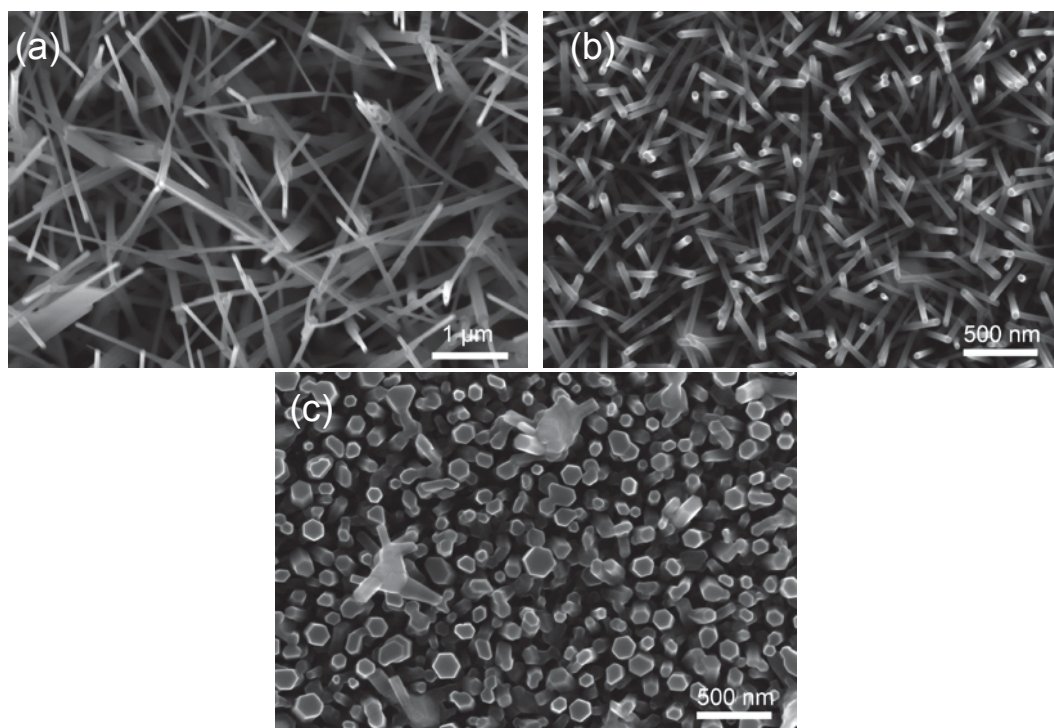


Figure 4.4. SEM images of ZnO nanowires grown at a source temperature of 950°C using Au films as the catalyst. (a) — (c): ZnO nanowires grown at temperatures of 950°C, 800°C and 700°C. The nanowires exhibit more regularly aligned structures with the decrease of the substrate temperature.

sufficient Zn vapour via carbothermal reduction. The substrates are placed downstream so that the Zn vapour deposition temperature can be varied by changing the location of the substrates, as shown in the furnace temperature profile in Figure 3.3(b). The spatial distribution of the vapour deposition sites affects the morphology of ZnO nanowires because they act as pedestals for the nanowire growth.

Figure 4.4 displays the morphology of ZnO nanowires grown at temperatures of 950°C, 800°C and 700°C, respectively. Needle-like nanostructures were formed when the substrate was placed at 950°C. These nanowires grown at 950°C show irregular alignment with a diameter of around 50 nm and a length of several microns. The

randomly aligned ZnO nanowires on the substrate should be related to the rugged surface after the annealing at 950°C, which exhibits irregular surface morphology. With the decrease of the growth temperature, the ZnO nanowires become larger in diameter and shorter in length. When the substrate temperature is reduced to ~700°C, the ZnO nanowires exhibit a diameter of ~200 nm and a length less than 1 μm . The decrease of nanowire diameter with increasing growth temperature suggests ZnO nanowires re-evaporate at 950°C under a low gaseous pressure [71].

4.2.3 Effects of pressure and flow of carrier gases

Table 4.3. Ranges of gas flow rates used for ZnO nanowire growth

Parameter Gas type	Flow rate (sccm)	Temperature at which O ₂ is introduced (°C)
Argon	20 — 100	25
Oxygen	4 — 15	700 — 900

The reaction between Zn vapour and the O₂ gas is reversible at high temperatures [96]. During the ZnO nanowire growth, Zn vapour is generated constantly from the carbothermal reduction when the source material reaches the reaction temperature. In the vapour-phase-transport (VPT) growth, the gaseous pressure in the reactor has notable influence on the morphology of ZnO nanowires [97], so it should be maintained constant. A proper ZnO nanowire growth requires an adequate pressure and an appropriate oxygen partial ratio in the ambient. In this work, the pressure and oxygen ratio in the reactor are controlled by adjusting the pumping speed as well as the

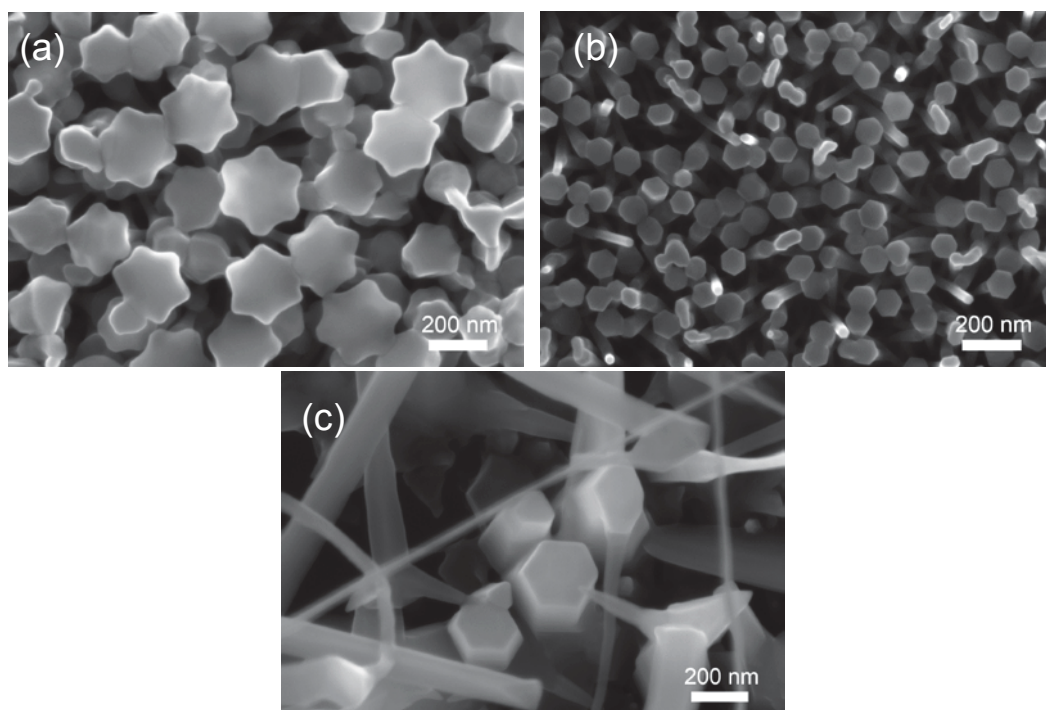


Figure 4.5. ZnO nanowires grown with O_2 introduced at different temperatures. (a) — (c): ZnO nanowires grown with O_2 introduced at temperatures of 700°C , 800°C and 900°C . The nanowires show tip hexagrams when O_2 was introduced at a lower temperature, while the introduction of O_2 at a higher temperature impedes the nanowires from growing longer.

Ar and O_2 gas flow rates. The gas control system was subsequently designed to allow the gas flow rate to be in the range of 10 to 100 sccm. The gas flow rate ranges for growing ZnO nanowires are listed in Table 4.3.

After the appropriate pressure and gas flow rate were achieved for the tube reactor, a flow of 5 sccm O_2 was introduced to initiate the nanowire growth. In this way, variations between growth experiments could be sufficiently reduced. To investigate the effects of oxygen source on the ZnO nanowire growth, the O_2 introduction temperature was changed while oxygen partial pressure was kept constant in this set of experiments.

The introduction of oxygen gas into the quartz tube, on one hand, provides the oxygen source which is indispensable for producing ZnO nanowires. On the other hand, oxygen gas reacts with graphite in the ZnO-C admixture, thus inhibits the carbothermal reaction. Early introduction of oxygen results in rapid oxidation of Zn vapour, thus reducing the availability of both Zn vapour and oxygen needed for the ZnO nanowire growth. As shown in Figure 4.5(a), when the oxygen gas is introduced into the reactor at 700°C, the grown ZnO nanowires possess thinner roots close to the substrate, while the nanowire tips form hexagrams at the later stage of the wire growth. Such nanowire shape is caused by the inconsistency of oxygen source at different growth stages. When O₂ was introduced at 900°C, the nanowires grow into hexagonal stubs with a length of ~200 nm and a diameter up to 300 nm. This phenomenon indicates that ZnO nanowires start to grow after the O₂ introduction at 900°C. The decrease in the average nanowire length should be due to the shortened growth time, considering that the furnace was kept at a constant heating rate and the overall reaction time was unchanged throughout the experiments.

4.2.4 Effects of Au film thickness

As shown in Figure 4.6(a), when 3 nm Au film was used as catalyst, the grown ZnO structures display the island morphology, similar to early stage growth of nanowires [see Figure 4.5(c)]. This is due to insufficient Zn vapour being deposited on the substrate. No obvious decrease in the average nanowire diameter is observed for Au film thickness in the range of 9 — 12 nm, which is consistent with previously reported nanowire growth using Au films [98]. The Au film for growing ZnO nanowires shown in Figure 4.6(b) is 12 nm in thickness. This type of Au nucleation sites immerse the nanowire root, which makes the nanowire growth procedure less stable thus

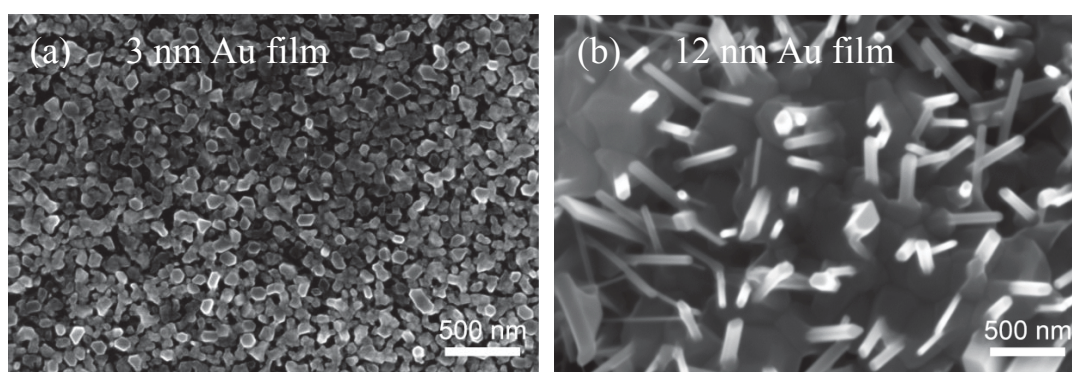


Figure 4.6. ZnO nanowires grown from Au layers of different thicknesses. (a) ZnO nanowires grown on the Si substrate coated with a 3 nm Au film. Less Zn vapour is deposited on the substrate with thinner Au layer used as the catalyst. (b) ZnO nanowires grown on the Si substrate with a 12 nm Au film. Excessive amount of Au causes the misalignment of ZnO nanowires.

affecting the wire alignment. For the ZnO nanowires grown using a Au film with thickness in the range of 9 — 12 nm, the melted Au completely covers the bottom of the nanowires and did not lead to an increase in nanowire diameter. Coating the substrate with a Au film provides a convenient method of depositing Au catalyst to initialise the wire growth. By setting the Au film to a suitable thickness, vertically aligned ZnO nanowires with high crystal quality can be obtained, which is an essential prerequisite for carrying out further investigations. However, due to the agglomeration of Au droplets caused by surface tension after the Au layer melts down, ZnO nanowire diameter can hardly be precisely controlled via changing the thickness of the Au catalytic layer, especially when the nanowires with particular sizes are required.

4.3 Diameter-controlled nanowire growth using Au nanoparticles

Although Au films have been widely used as catalyst for growing ZnO nanowire, this method has a major disadvantage that the formation of Au droplets by post-annealing

and their size distributions are not precisely controllable. Uniform size of catalyst droplets is largely demanded for the growth of regular, high quality nanowires. Au nanoparticles, especially the ones as small as 5 nm, are more controllable and provide an alternative route for growing nanowires with controlled diameters. The amount of Au in the particle form can be more accurately adjusted by properly diluting the Au nanoparticle colloid into suspensions with different concentrations. Poly-L-lysine is widely used for charging the substrates positive in order to deposit various types of negatively charged particles. According to previous studies, in order to prepare positively charged substrate for Au nanoparticle absorption, the silicon or sapphire could be functionalised using poly-L-lysine and rinsed afterwards so that no residuals are left on the substrate surface [87, 99]. In this project, the influence of growth parameters on the dimensions and defect formation in ZnO nanowires was investigated.

In the case of VS growth, ZnO nanowires orientated along the *c*-axis of the wurtzite crystal can be described as alternating stacking planes of tetrahedrally coordinated O²⁻ and Zn²⁺ ions, with the growing *c*-facet being either O- or Zn-terminated surface [100]. These uncompensated polar surfaces carry net positive or negative charges; their electrostatic interactions are known to play a critical role in the formation of nanohelices, nanobelts and nanosprings [101]. For example, the electrostatic forces in nanobelts result in coaxial coiling and the ZnO growth along $[10\bar{1}0]$ direction [102]. Spectral CL imaging is a powerful method to investigate the spatial distribution of luminescence centres in ZnO nanostructures [103]. In this project, this technique has been successfully applied to investigate the merging phenomenon, revealing remnants of the original crystalline structure within coalesced nanowires. The diameter and

density of semiconductor nanowires can be modulated via the control over the density of catalytic Au nanoparticles.

Although merging effects have been observed in the nanowire growth via the VLS and VS mechanisms, the physical mechanisms contributing to the merging are different. For the VLS nanowire growth, the diameters of nanowires are governed by the size of the Au droplets at the tip of the nanowires [104]. The merging of two nanowires occurs at the tips of these nanostructures which are covered with Au nanodroplets. The merged Au droplet then absorbs source vapour and guides the wire grow. Such tip Au droplet merging phenomenon can be explained by the Ostwald ripening theory [105].

While for the VS nanowire growth mechanism, the diameters of nanowires are primarily determined by the proximity of dispersed Au nanoparticles [88], and the adjacent nanowires will combine into one nanowire when the nucleation sites are close to each other [88]. This discovery also indicates that merging effects will hardly occur if the nucleation sites are too sparsely distributed on the substrate. Two nanowire merging phenomenon during the GaAs nanowire MOCVD growth is reported to be caused by the Coulomb interaction between polar surfaces of two adjacent wires, which was properly interpreted by analysing the induced mechanical energy using the Euler-Bernoulli beam theory [16].

In the ZnO nanowire growth via the VLS mechanism, the diameter of nanowires grown from catalytic nucleation sites is in direct proportion to the size of Au nanoclusters rather than the size of Au nanoparticles because of the supersaturation of the material vapour on the Au nucleation sites [106]. The MOCVD grown GaN nanowires with uniform diameter were realised by using a holey mask to cover the substrate during the

vapour deposition [107]. While in the condition without the mask constraint, the stability of catalytic Au nanoparticles on the substrate becomes critically important.

4.3.1 Assembly of Au colloidal nanoparticles on substrate

The dispersed 5 nm Au nanoparticles using the solution with different dilution rates are shown in Figure 4.7. Figures (a) — (i) exhibit the morphology of Au nanoparticles anchored on Si substrates using the electrostatic deposition from the solutions with the indicated Au nanoparticle concentrations from 5.5×10^{12} particles/mL to 5.5×10^{13} particles/mL. Because of their small size, the 5 nm Au nanoparticles possess a high surface-to-volume ratio and can be evenly dispersed on the substrate. The Au particles on the substrates become more densely distributed from 5×10^{12} particles/mL to 5.5×10^{13} particles/mL, as evidenced by SEM images from Figure 4.7 (a) to (i). All the spread Au nanoparticles exhibit even coverage on the substrates and no particle agglomeration occurs during the suspension dispersion, indicating that the Si substrates carry evenly distributed positive charges and the 5 nm Au nanoparticles possess same amount of negative charges. After adding MilliQ water into the colloid, the Au nanoparticles remain in the suspension and no precipitation is formed, which confirms that MilliQ water is an appropriate solvent for diluting Au colloid.

In order to examine the dependence of the density of catalytic Au nanoparticles on the Au particle concentration in the colloidal suspension, the density of Au particles adhering on the silicon substrate was calculated by counting the Au particles shown on the high-resolution SEM images. As displayed in Figure 4.8, the Au nanoparticle density increases from 30 particles/ μm^2 for the Au colloidal concentration of 5.5×10^{12} particles/mL to above 200 particles/ μm^2 for 5.5×10^{13} particles/mL. The

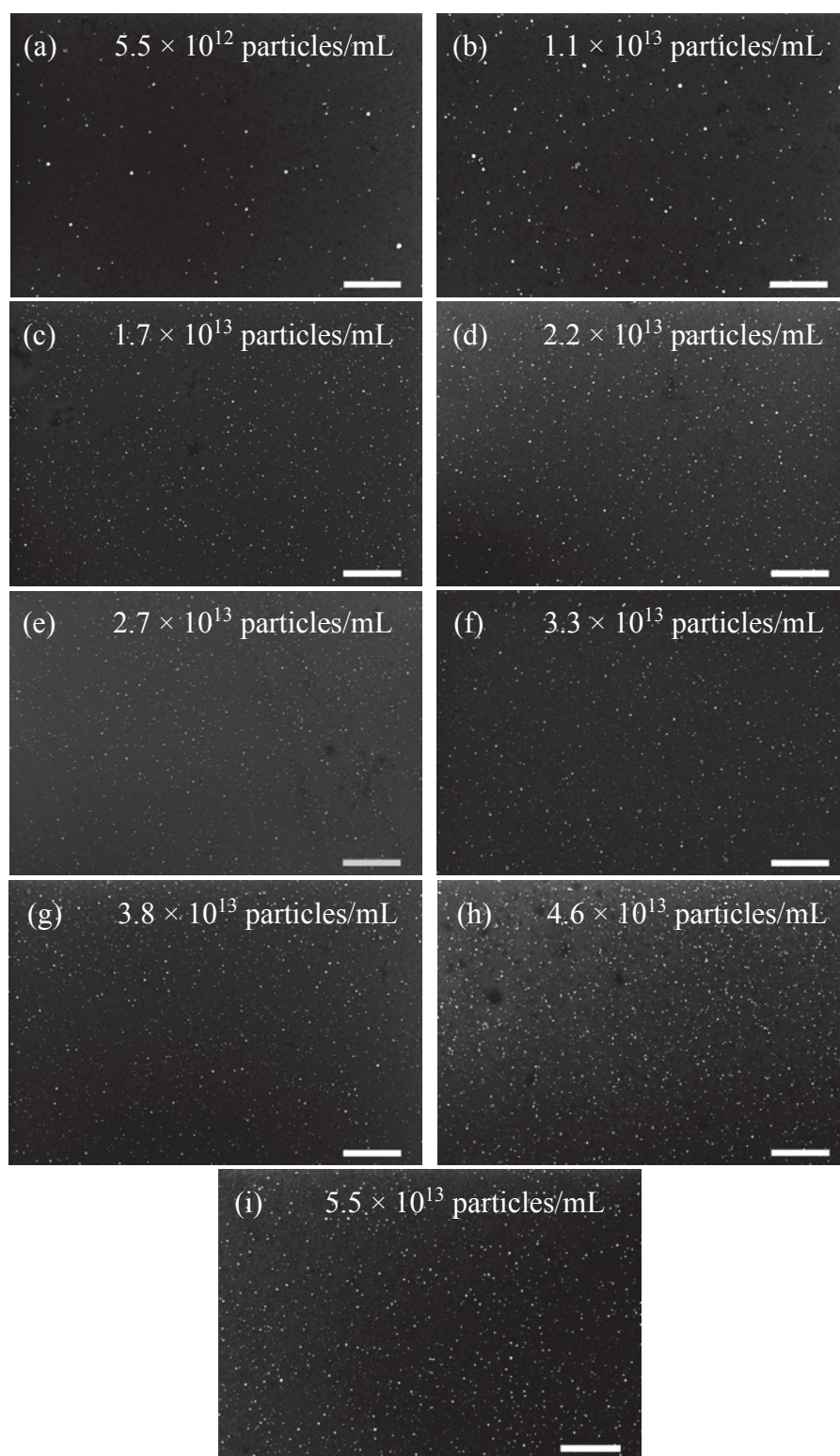


Figure 4.7. 5 nm Au nanoparticles deposited onto Si substrate using the electrostatic assembly method. Dispersed Au nanoparticles using the colloidal suspensions with different Au concentrations denoted on the images. The scale bar in each image represents 500 nm.

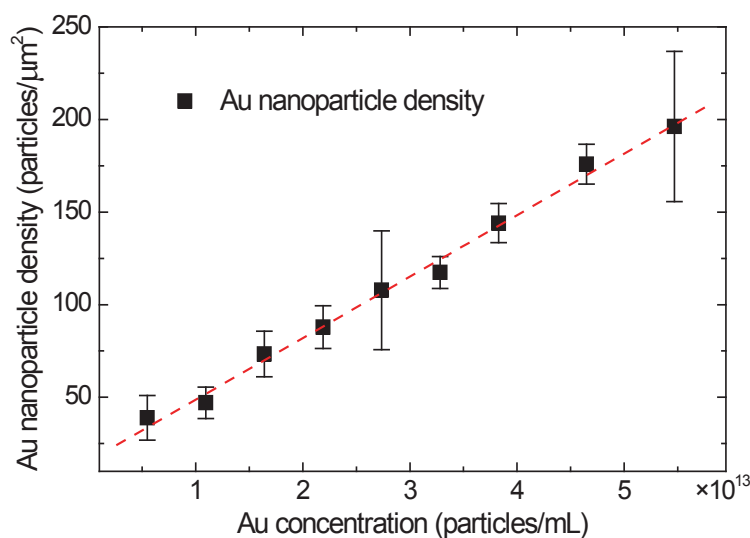


Figure 4.8. Dispersed Au particle density on the substrate versus Au nanoparticle concentration in colloidal solution. The Au nanoparticle density on the silicon substrates is proportional to the Au particle concentration in the colloidal suspension. The error bars represent one standard deviation.

error bars represent one standard deviation of the Au nanoparticle density by counting ten images for each Au colloidal concentration. The fitted line shows that the density of Au nanoparticles adhering to the Si substrates exhibits almost linear dependence on the Au suspension concentration.

4.3.2 Morphology of ZnO nanowires grown from Au nanoparticles

Figure 4.9 shows the ZnO nanowires obtained by using the Au nanoparticle covered Si substrates, as displayed in the template images in Figure 4.7. As a general trend, a higher density of catalytic Au nanoparticles leads to ZnO nanowires of larger diameters. The absence of Au nanoparticles at the tip area confirms that ZnO nanowires grow via the VS mechanism [99]. All the ZnO nanowires possess a hexagonal basal *c*-facet at the tips, which has the highest surface energy and can drive the nanowire growth [108].

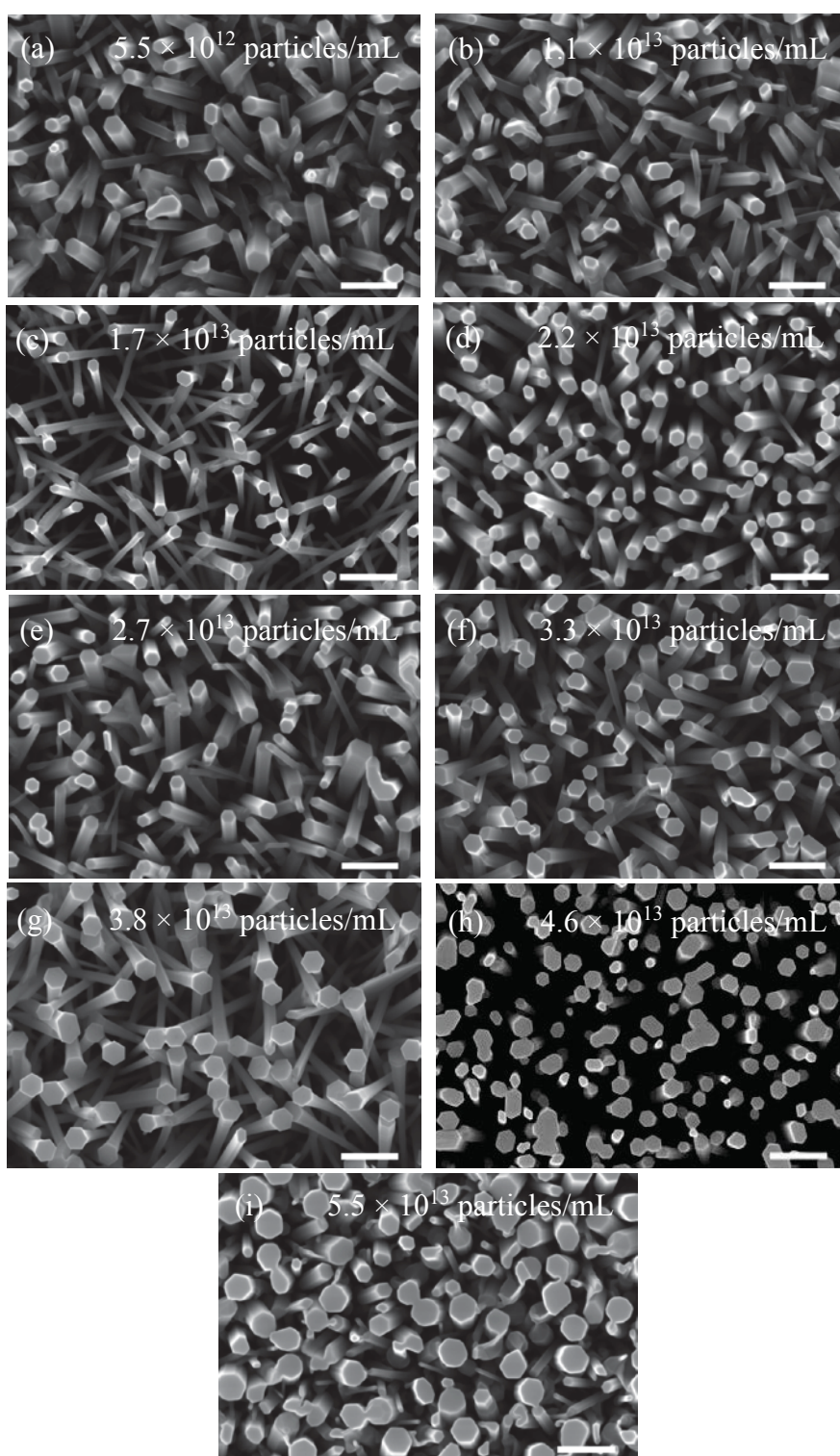


Figure 4.9. SEM images ZnO nanowires grown using 5 nm Au nanoparticles via the VS mechanism ($E_B = 10$ keV). The colloidal nanoparticle concentrations are displayed on the images. The scale bar represents 500 nm for each image.

With the variation of the Au nanoparticle concentration, the grown ZnO nanowires exhibit slightly different shapes along their growth direction. Figure 4.9 (c) and (g) show that nanowires have smaller diameter at the root, while the nanowire diameters in other images are constant along the length. The slightly nanowire diameter expanding towards the tip could be due to the larger amount of Zn vapour and oxygen source available to the wire tip facets than to the wire roots. In addition, the laminar gas flow at the nanowire tips is considered to be more stable than the root, because the possible turbulent gas flow between the growing wires may reduce the amount of source material close to the bottom area [109].

It is noteworthy that the coincident wire merging by tip-touching is rare among all of the nanowires shown in Figure 4.9, although some wires grow at certain angles to the substrates. This indicates that the ZnO nanowire merging and coalescing effects are

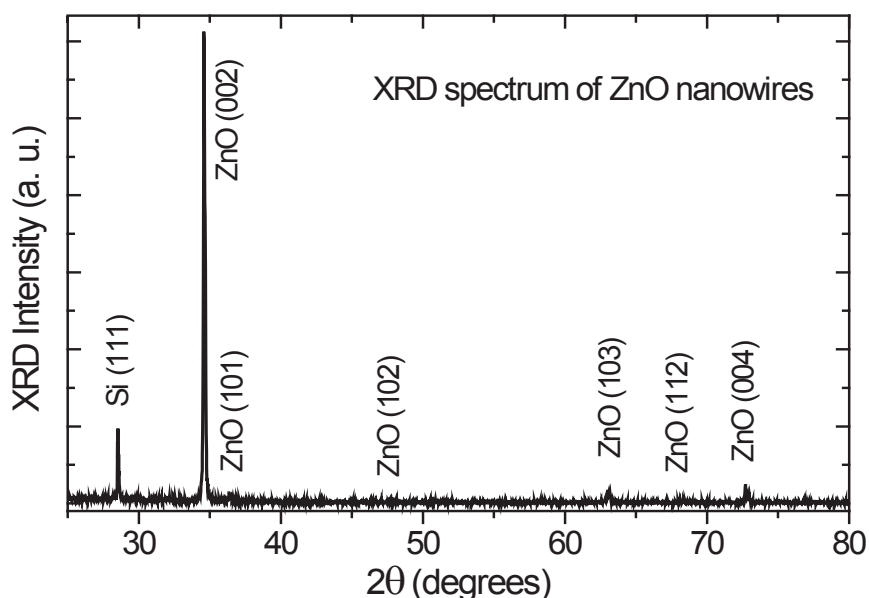


Figure 4.10. XRD spectrum of ZnO nanowires grown from 5 nm Au colloidal nanoparticles with a concentration of 5.5×10^{13} particles/mL. The dominant ZnO (002) peak shows that the ZnO nanowires grow preferentially along the *c*-axis.

following a specific set of rules, which are related to the wire shape and the mechanical forces between wires.

XRD analysis confirms that ZnO nanowires are grown along the *c*-axis orientation (Figure 4.10). Si peak is significantly suppressed after the wire growth, indicating that the densely grown ZnO nanowires are almost uniformly distributed on the sample surface. No Au XRD pattern is shown in Figure 4.10, while a relatively strong Au(111) peak is observed in the XRD spectrum of the ZnO nanowires grown using Au layer as the catalyst, as displayed in Figure 5.3. The missing of the Au pattern in the Au nanoparticle grown ZnO nanowires indicates that the amount of Au in this method is much less than the growth done by using Au catalytic film.

4.3.3 Dependence of nanowire diameter on Au colloidal concentration

To illustrate the relationship between the Au nanoparticle concentration and ZnO nanowire dimensions, histograms of nanowire diameters were obtained by measuring around 400 nanowires on each substrate. The nanowire diameter distribution can be fitted using a Gaussian function, which yields mean diameters of 111 ± 12 nm and 193 ± 36 nm for ZnO nanowires grown using 2.2×10^{13} and 4.6×10^{13} Au nanoparticles/mL, respectively [Figure 4.11(a) and (b)]. With the increase of the Au nanoparticle concentration, the mean diameter of ZnO nanowires is enlarged from 97 ± 32 to 222 ± 24 nm as the Au concentration increases from 2.2×10^{13} to 5.6×10^{13} particles/mL. Meanwhile, the nanowire density drops from ~ 11 to 6 wires/ μm^2 , as shown in Figure 4.12. The mean nanowire diameter shows different behaviour with the increase in Au nanocatalyst concentration: below 2.2×10^{13} Au nanoparticles/mL, the

nanowire diameter is statistically unchanged; while above 2.2×10^{13} Au nanoparticles/mL, the diameter of ZnO nanowires increases almost linearly with the

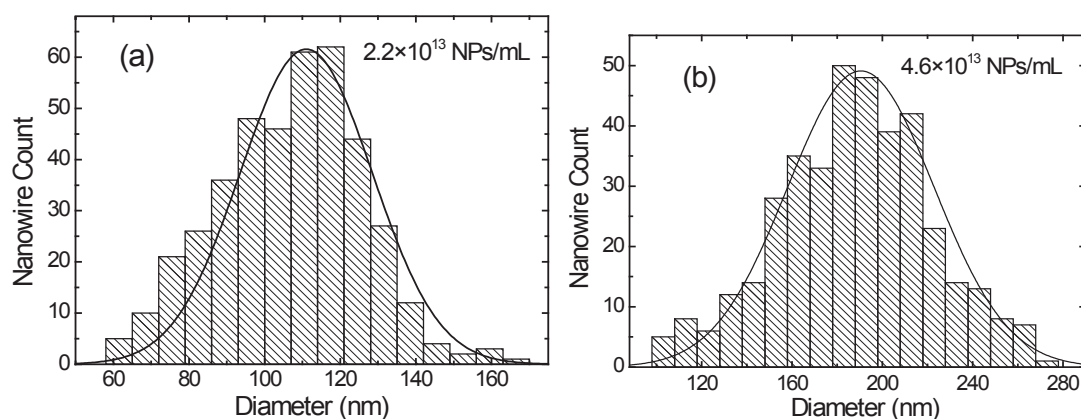


Figure 4.11. Histograms of diameters for ZnO nanowires grown from catalytic Au nanoparticles dispersed on Si substrates. The colloidal Au concentrations are indicated in the histograms. The curves represent fitted Gaussian distribution, which yields mean diameters of (a) 111 ± 12 nm and (b) 193 ± 36 nm.

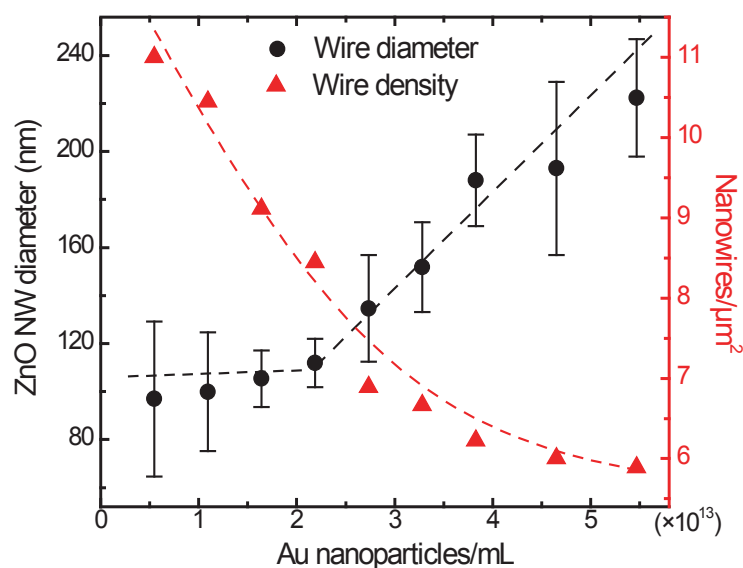


Figure 4.12. ZnO nanowire diameter and nanowire density as a function of Au colloidal concentration. The black circles and the red triangles represent the diameter and density of ZnO nanowires, respectively. The error bars indicate the standard deviation.

Au concentration. The increase in the nanowire diameter indicates coalescence of thinner ZnO nanowires during growth as the Au catalytic sites on the substrate become denser and the nanowire separation reaches a threshold distance.

4.3.4 ZnO nanowire bending and cantilever model

To investigate the role of Au nanocatalysts in the growth of ZnO nanowires, Au nanoparticles were deposited through a shallow mask, producing a patterned layer of Au. This patterned template was subsequently used to grow ZnO nanowires. No ZnO nanowires were found in the Au-free regions of the template, as shown in Figure 4.13(a), indicating that Au catalytic nanoparticles are a prerequisite for ZnO growth. The

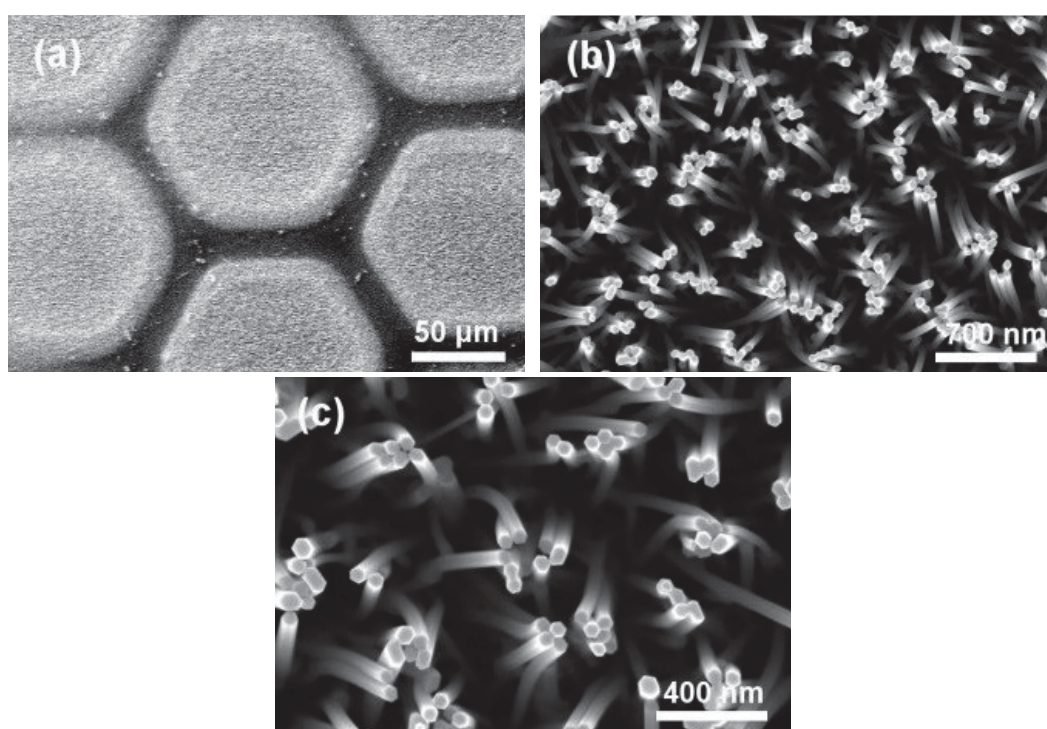


Figure 4.13. ZnO nanowires grown from patterned Au layer and the wire tip-merging. (a) No ZnO nanowires were grown on the sites without Au, indicating the Au catalytic nanoparticles are pivotal to the VS-growth of ZnO nanowires. (b) and (c) display SEM images of different magnifications showing nanowires to merge and coalesce after reaching a critical length.

bending of ZnO nanowires are more clearly observed in the SEM images of truncated nanowires at different magnifications [Figure 4.13(b,c)] after ultrasonication in isopropanol, which broke the nanowires close to the merging intersection. SEM observations show that many nanowires of length greater than ~ 400 nm are bent and attracted to each other at their tips to form bundles of various numbers of nanowires. Close examination of SEM images for cleaved samples reveals some nanowires do not merge with adjacent ones but bend further away to contact with distant wires, indicating the existence of both attractive and repulsive forces.

Polar surfaces of many ionic crystals are unstable and undergo reconstruction to minimise surface energy. ZnO is an exceptional semiconductor, where both clean (0001)-Zn terminated and (000 $\bar{1}$)-O terminated surfaces have been shown to be remarkably stable [110]. The bending of VS-grown ZnO nanowires during growth can be attributed to the polar *c*-facets of ZnO nanowire tips, which induce long-range Coulomb interactions between the nanowires. This electrostatic interaction mechanism is consistent with the absence of coalesced tips in VLS-grown ZnO nanowires as no strong Coulomb force exists between nanowires when Au droplets sit on top and cover the polar faces of nanowires.

The CL spectral image of the cross-sections of coalesced ZnO nanowires is shown in Figure 4.14(a) with the schematic illustration displayed in Figure 4.14(b). This CL image is colour-coded to indicate regions of strong green ($\lambda = 500$ nm) and ultra-violet (380 nm) emissions in the merging region, where the bending nanowires start to coalesce. The nanowires in Figure 4.14(a) consist of multiple constituent nanowires (highlighted by the dashed hexagons), which are clearly distinguishable by the remnant

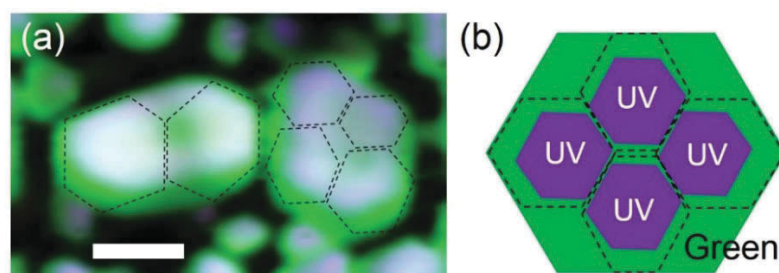


Figure 4.14. CL spectral image of fused ZnO nanowires that originates from several smaller incipient nanowires, as displayed in (a). The scale bar represents 200 nm. The core of the coalesced nanowires contains multi-crystalline structure with enhanced sidewall-related green emission remaining inside these nanowires. (b) Illustration of strong ultraviolet (UV) luminescence at the core of incipient nanowires and remnant green luminescence at the interface between merging nanowires.

sidewall-associated green emission that remains inside these large coalesced nanowires. The green emission arises primarily from the a -plane sidewalls of the nanowires, while the UV luminescence dominates the nanowire core [83]. The remnants of the constituent nanowires were not completely annealed out during the short growth process. The green boundary of the coalesced nanowire is significantly larger than the remnant green region between the constituent nanowires as the crystallisation of the core takes place, driven by lower system free energy.

The density of coalesced ZnO nanowires is dependent on the concentration of the Au nanocatalysts, which determines the mean nanowire separation, d . The fundamental assumption for analysing nanowire bending and coalescing is that the size of the metal catalyst determines the diameter of the incipient nanowires. When ZnO nanowires are far apart from each other, the electrostatic force between wires is negligible and the average nanowire diameter remains constant and is independent of Au colloidal concentration, as shown in Figure 4.12. When ZnO nanowires are close together,

however, the Coulomb force between $\{0001\}$ and $\{000\bar{1}\}$ polar end faces increases rapidly as $\sim 1/d^2$. Nanowire tips with the same polarity repel each other while those carrying opposite charges start to attract each other and coalesce to form a single fused nanowire with a larger diameter.

The increased Au nanoparticle density on the substrate reduces the average distance between individual incipient nanowires, decreasing the number of nanowires per unit area as more wires merge and coalesce. Thin nanowires have smaller moment of inertia and their mechanical stiffness can be easily overcome by the Coulomb forces between nanowires. While for thicker nanowires, the mechanical force needs to be overcome surpasses the Coulomb force, so no bending and coalescence occur. To elucidate the nanowire merging, the surface-charged ZnO nanowire is considered as a cantilever with an electrostatic force exerted on the free end. The geometrical (nanowire radius r , separation d , length L) and electrostatic forces used to describe the three-nanowire bending model are depicted in Figure 4.15. In this model, the tip of nanowire A possesses a negatively charged surface while nanowires B and C carry positive charges. Suppose a force F is acting on the free end of a nanowire cantilever, according to the

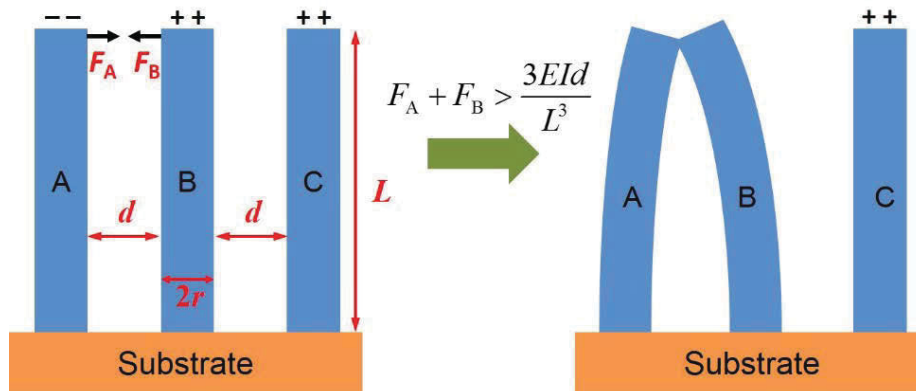


Figure 4.15. Schematic of nanowire bending model due to Coulomb forces between growing c -facets of VS-grown ZnO nanowires.

Euler-Bernoulli beam theory [111], the deflection at the end of the cantilever, w , can be expressed as:

$$w = \frac{FL^3}{3EI} \quad (4.1)$$

where E is the elastic modulus of ZnO and I is the moment of inertia for a hexagonal beam, $I = (5\sqrt{3}/16)r^4$. The bending and coalescence of ZnO nanowires occur at specific stages of the growth when nanowires reach an appropriate length. For nanowires A and B to make contact, their deflection at the free end must be larger than their separation, d :

$$w_A + w_B = \frac{F_A L^3}{3EI} + \frac{F_B L^3}{3EI} > d \quad (4.2)$$

Given the high aspect ratios of the nanowires, the tips can be modelled as a point charge, $Q = (3\sqrt{3}/2)r^2 \cdot \sigma$, where σ is the surface charge density. Hence, the electrostatic forces acting on the free end of nanowires A and B can ultimately be written as:

$$F_A = k \frac{Q^2}{d^2} + k \frac{Q^2}{(2d)^2} = k \frac{135r^4 \cdot \sigma^2}{16d^2} \quad (4.3)$$

$$F_B = k \frac{Q^2}{d^2} + k \frac{Q^2}{d^2} = k \frac{27r^4 \cdot \sigma^2}{2d^2} \quad (4.4)$$

Substituting F_A and F_B into (4.2) gives an estimate of the nanowire surface charge required to bend nanowires:

$$\sigma > \frac{d}{3L} \sqrt{\frac{5\sqrt{3}Ed}{13kL}} \quad (4.5)$$

For the ZnO nanowire system shown in Figure 4.15 with average wire length $L = 400$ nm, distance $d = 50$ nm, and ZnO elastic modulus $E = 29$ GPa [112], the minimum

charge density required is $\sigma_{\min} = 0.022 \text{ C/m}^2$. This value is of the same order of magnitude as the spontaneous polarisation of bulk ZnO obtained from *ab initio* calculations (0.06 C/m^2) [113]. The calculation based on this qualitative model thus supports the electrostatic interaction mechanism that drives the bending of nanowires.

4.3.5 Oxygen vacancy defects in ZnO nanowires

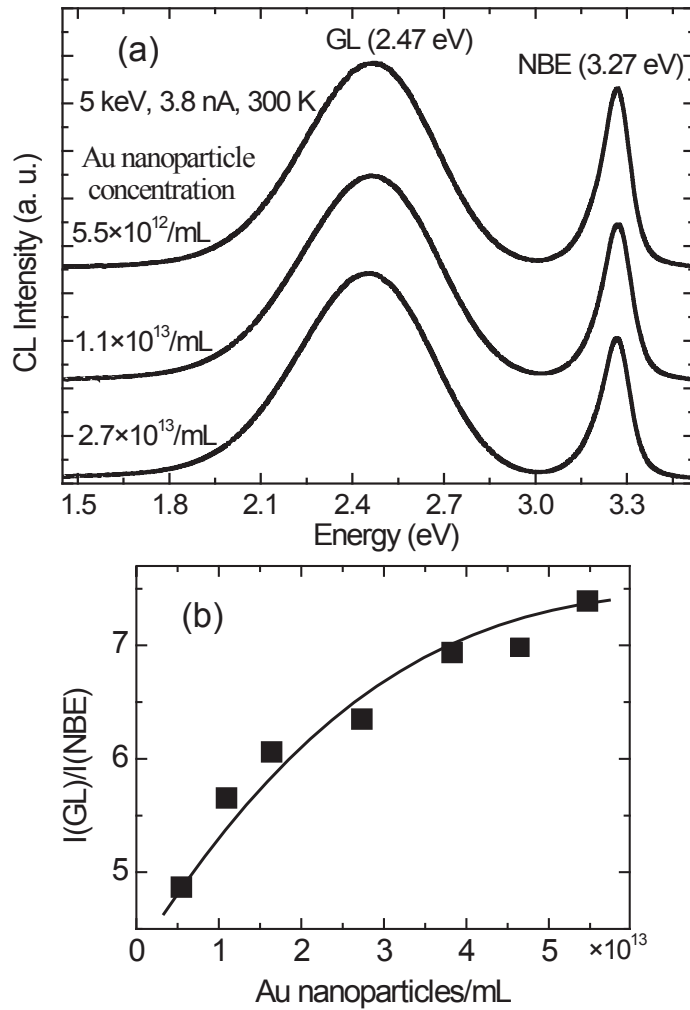


Figure 4.16. CL spectra of ZnO nanowires grown from Au nanoparticles and the intensity ratio $I_{\text{GL}}/I_{\text{NBE}}$ versus the Au concentration with the Au particle suspensions at different colloidal concentrations (CL scan area = $9 \mu\text{m}^2$), as shown in (a) and (b), respectively. GL emission is enhanced with the increase in Au nanoparticle concentration. The integrated intensities were acquired by fitting each CL spectrum into two Gaussian peaks.

An important aspect of ZnO nanowire growth in this approach is the dependence of defect formation on the density of Au catalytic nanoparticles. Figure 4.16(a) shows that CL spectra of the nanowires, which exhibit two main luminescence features: a sharp NBE emission at 3.27 eV and a symmetrical green luminescence (GL) peak at 2.47 eV, which has been proved to be related to oxygen vacancy (V_O) defects [114]. To investigate the role of catalytic Au, the relative integrated intensity of the V_O -related GL is plotted as a function of Au nanoparticle concentration [Figure 4.16(b)]. The intensity ratio I_{GL}/I_{NBE} rises monotonously from 4.8 to 7.4 over the Au concentration range used in this study, indicating an increase in V_O defect concentration. This defect density dependence on nanowire diameter can be explained by the annihilation kinetics of defects during high-temperature growth, in which V_O defects in small ZnO nanowires are annealed out more readily than in large nanowires.

4.4 Summary

In conclusion, ZnO nanowires have been grown via the VS mechanism by using Au catalyst. An effective ZnO nanowire growth method was established. Coating the substrate with Au film provides a convenient method of depositing Au catalyst to initialise the wire growth. Au layer breaks into tiny droplets prior to the precipitation of the Zn vapour. Vertically aligned ZnO nanowires with high crystallinity and finite diameter can be obtained by depositing a thin Au layer with proper thickness. Thin, flexible ZnO nanowires were grown from 5 nm Au nanoparticles and their close proximity to each other leads to significant electrostatic interactions causing the nanowires to bend and coalesce to form nanowires of larger diameters. This merging phenomenon leads to both the density and structural quality of ZnO nanowires highly dependent on their integration density on the substrate. The width of the ZnO nanowires

becomes larger as the density of Au nanoparticles increases. Some remnant of green luminescence from the *a*-plane sidewalls of constituent nanowires were found within the coalesced nanowire. A nanowire bending model is established by investigating the Coulomb forces between the *c*-facets of nanowires. Optical characterisation shows that larger nanowires contain more oxygen vacancies than smaller ones. ZnO nanowires of different diameters can be grown using colloidal Au nanoparticles by simply controlling the Au nanoparticle concentration, which can provide a new route for obtaining diameter-controllable 1D ZnO nanostructures.

Chapter 5 Nitrogen dopants in ZnO nanowires

5.1 Introduction

To date, no experimental study has examined the interrelationships between the chemical states of nitrogen dopants and the optical signatures of shallow acceptors. In this study, opto-electronic properties of ZnO nanowires doped with specific nitrogen species are investigated. Nanowires were specifically chosen for this study as these low dimensional structures enable control over the formation of native defects during growth as well as uniform doping of nitrogen throughout their entire volume.

In this thesis, two different approaches have been applied to incorporate nitrogen into ZnO nanowires. In the first approach, N₂O dopant gas is introduced during the nanowire growth and the nitrogen is incorporated into ZnO nanowires during their growth. In the second approach, nitrogen is ionised in a radio-frequency plasma chamber and is incorporated into ZnO nanowires in post-growth annealing. With the application of a rf plasma generator, the as-grown ZnO nanowires are annealed in ionised nitrogen environment and nitrogen can be incorporated into the entire nanowire given its small dimension.

5.2 *In-situ* growth of N-doped ZnO nanowires

5.2.1 *In-situ* doping using N₂O gas

Nitrous oxide (N₂O) is a colourless gas with chemical bond structures of N≡N–O or

$\text{N}=\text{N}=\text{O}$. Among these two chemical structures, the latter one has a $\text{N}=\text{N}$ double bond, which possesses lower bond energy than the $\text{N}\equiv\text{N}$ triple bond. The nitrogen species in $\text{N}=\text{N}=\text{O}$ are more likely to dissociate from the N_2O and form chemical bonds with the ZnO host lattice, so the N_2O gas in the form of $\text{N}=\text{N}=\text{O}$ has the potential to incorporated nitrogen acceptors into ZnO when being introduced *in-situ* as the dopant gas during the VPT nanowire growth. In this work, for growing *in-situ* N-doped nanowires, N_2O was introduced into the reactor during the vapour deposition at a gas flow rate between 2 and 10 sccm.

5.2.2 Morphological properties of *in-situ* N-doped ZnO nanowires

The grown ZnO nanowires were found to be vertically aligned and have well-defined hexagon-shaped facets, as shown in Figure 5.1. The typical length is about 1 μm while the diameter varies in the range of 70 — 110 nm. The hexagonal symmetry of the nanowires suggests that the high crystalline quality is barely influenced by the lattice mismatch of ZnO and the supporting substrate. The introduction of N_2O did not induce significant changes in size or shape of the nanowires, although the wires slightly shrink in diameter with the increase of the N_2O gas flow rate, indicating the subtle interference of the *in-situ* introduced N_2O gas on the growth environment.

Figure 5.2 shows average diameters of the undoped and N-doped ZnO nanowires with different amounts of N_2O introduced during the nanowire growth. The statistics were attained by counting the undoped and N-doped nanowire diameters, as displayed in Figure 5.1(a) — (f). The average diameter of ZnO nanowires follows a decreasing trend with more N_2O used as the dopant gas. As shown in Figure 5.2, the undoped ZnO nanowires and the N-doped ZnO nanowires using small amount of N_2O exhibit

similar average diameters; while the nanowire diameter decreases from 140 nm to 80 nm with the N_2O gas flow rate increasing from 2 sccm to 10 sccm, indicating that the *in-situ* N_2O dopant gas with a flow rate higher than 2 sccm will interfere during the ZnO deposition via the formation of N-related chemical bonds.

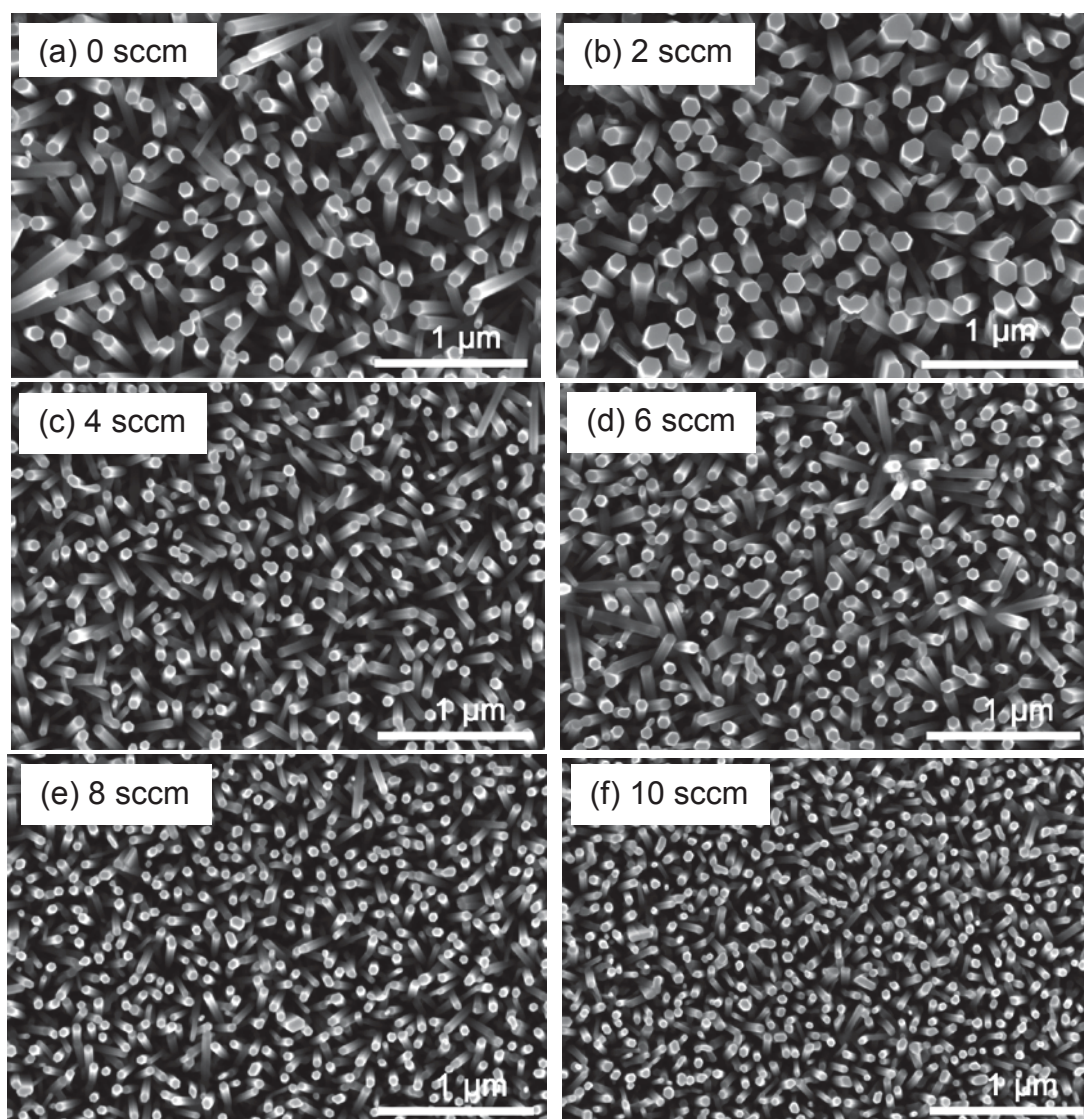


Figure 5.1. SEM images of ZnO nanowires grown using different N_2O gas flow rates. (a): As-grown ZnO nanowires; (b) — (f): ZnO nanowires grown with the dopant N_2O gas introduced *in-situ* and the N_2O gas flow rates are denoted on corresponding images. The nanowires are vertically aligned on the Si substrates and their diameters slightly decrease with more N_2O gas used for the growth, indicating the subtle interference of N_2O gas on nanowire morphology.

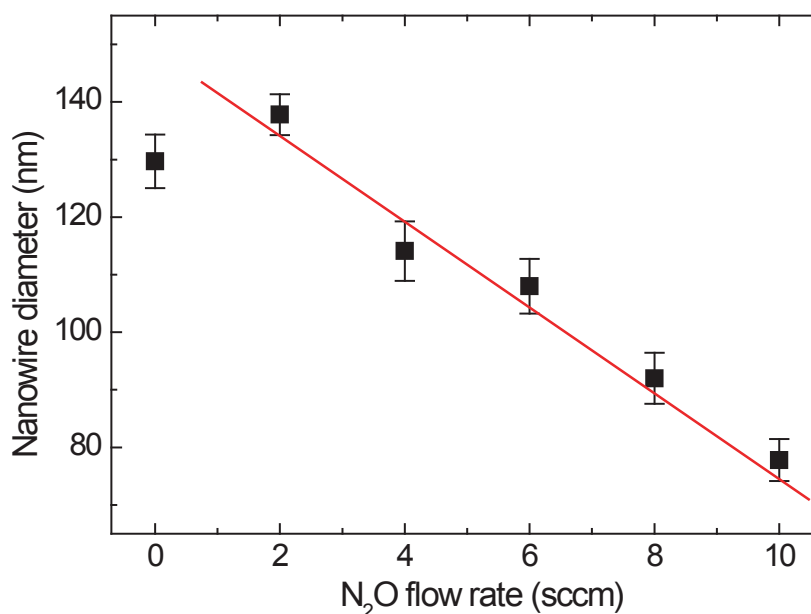


Figure 5.2. Diameter of undoped and N-doped ZnO nanowires with different amounts of N₂O used as the dopant source. The error bars represent the standard error.

5.2.3 Crystal structure of N-doped ZnO nanowires

Figure 5.3 shows typical XRD (θ -2 θ) spectra of undoped and N-doped ZnO nanowires using different N₂O gas flow rates. All of these six spectra are dominated by the intense (002) reflection at 34.5°. The second prominent feature from ZnO is the (004) diffraction at 72.6°, which is the second order of the (002) reflection. While the other ZnO diffraction peaks, such as (101), (102) and (103), are weak, indicating that the nanowires are highly crystalline and were predominantly grown along the *c*-axis of the wurtzite lattice structure.

Si(111) diffraction at 28.4° indicates the reflection of the Si(111) substrate. Au(111) at 38.5° is also detectable in the diffractograms showing the presence of the crystallised Au droplets due to the melting down of the continuous Au catalyst layer. The intensity of Au(111) in each XRD spectrum is found to be affected by the morphology of the

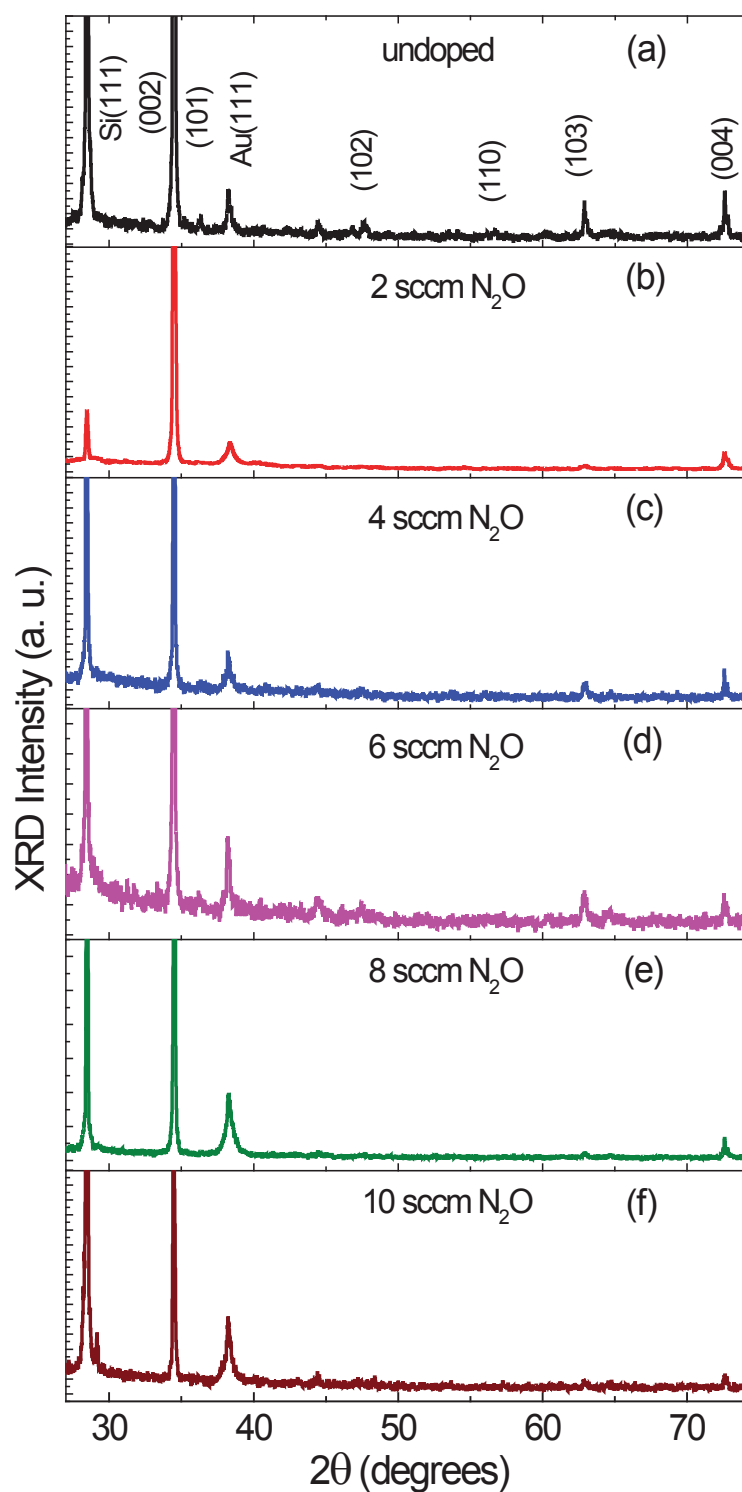


Figure 5.3. XRD patterns of undoped and N-doped ZnO nanowires using N₂O. (a): XRD spectrum of undoped ZnO nanowires; (b) — (f): XRD spectra of N-doped ZnO nanowires with N₂O gas flow rates of 2, 4, 6, 8 and 10 sccm. The dominance of (002) peak indicates most nanowires prefer to grow along the *c*-axis with the growth direction perpendicular to the substrate surface.

ZnO nanowires. For the nanowires distributed more sparsely on the sample surface, the X-ray exhibits stronger diffraction at Au(111) mode. The effects of N incorporation on the microstructure of nanowires are sufficiently small and no significant changes were detected by XRD.

5.2.4 Raman modes associated with atomic N and molecular N₂

5.2.4.1 Review of nitrogen Raman modes in ZnO

Table 5.1. Assignments of N-related Raman modes in ZnO

Raman shift (cm ⁻¹)	Assignment	Reference
~275	Zn _I -N _O complexes; N _O	[51]
~437	E ₂ (high) of ZnO (key signature of ZnO)	[115]
570	Overlapping N-related bands	[116]
~575	A ₁ (LO), enhanced by substitutional N atoms and/or N-H complexes on O sites	[117]
~580	N _O	[115]
~642	N-related complex defects	[116]
~856 (weak)	N-related, cause is unclear, only detectable in parallel polarisation	[115]
~2253 (weak)	lattice-bound nitrogen or complexes	[118]
~2277 (weak)	lattice-bound nitrogen or complexes	[118]
2291 (strong)	lattice-bound nitrogen or complexes	[118]
~2300 (broad)	4LO multiphonon scattering, induced by extrinsic impurities, such as ion implantation	[119]
2306 (sharp)	nitrogen related complexes	[119]
2329	N ₂ vibration in air	[118]

Table 5.1 lists the N-related Raman modes in ZnO, as have been reported so far. Raman scatterings at 275, 510, 582, 643, and 856 cm^{-1} are the proposed nitrogen modes in ZnO, which correlate linearly in intensity with nitrogen concentration, as previously reported by Kaschner *et al.* [115]. Experimental and theoretical results all support that the Raman scattering peak at $\sim 273 \text{ cm}^{-1}$ is related to the existence of Zn_i , but the role of nitrogen in the formation of Zn_i or its complexes is still unclear [51, 120]. The Raman mode at 576 cm^{-1} was ascribed to the resonant multiple longitudinal optical (LO) phonon scattering induced by defects [117]. The nitrogen-related Raman vibrations at 2253, 2277 and 2291 cm^{-1} could be ascribed to the presence of molecular nitrogen species in ZnO, taking into account their proximity in wavenumber to the Raman scattering of N_2 gas in air [118].

5.2.4.2 Raman vibrations of *in-situ* N-doped ZnO nanowires

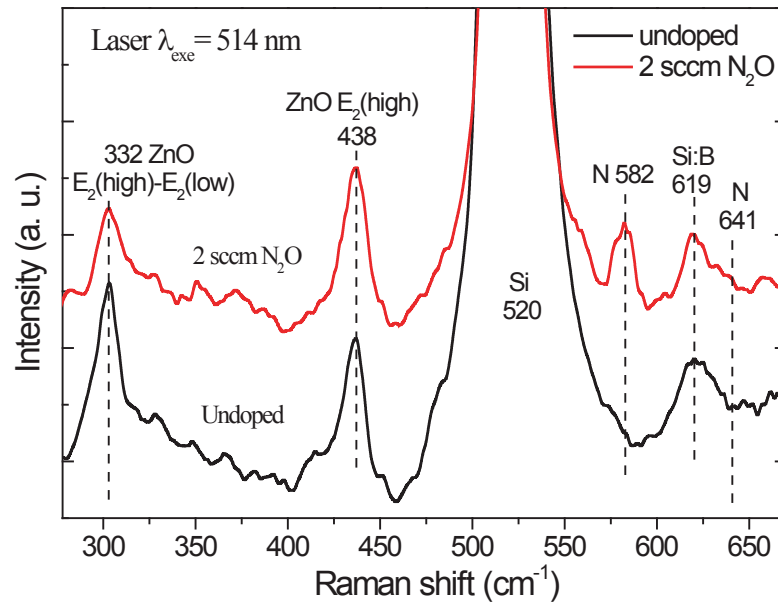


Figure 5.4. Raman spectra of as-grown and N-doped ZnO nanowires grown using 2 sccm N_2O as the dopant gas. The N-related Raman peak at 582 cm^{-1} emerges after N-doping, while the additional mode at 642 cm^{-1} only exhibits minor increase in the N-doped ZnO nanowires.

Figure 5.4 shows typical Raman spectra of undoped and N-doped ZnO nanowires. As the spectra were collected in the backscattering geometry, E_2 and $A_1(\text{LO})$ modes are active while $E_1(\text{LO})$ is forbidden [121]. Both spectra are dominated by the intense peak at 529 cm^{-1} arising from the excitation of the Si substrate, while the weak peak at 619 cm^{-1} is likely due to boron impurities in Si [122]. These Raman features are detectable due to the high transmittance of ZnO at the selected laser wavelength (514 nm). For both N-doped nanowires and the undoped reference, the significant feature is the $E_2(\text{high})$ phonon mode of ZnO at 438 cm^{-1} . Additional Raman peaks at 580 and 642 cm^{-1} , previously assigned to nitrogen local vibrational modes by other researchers [115], were found in N-doped nanowires, but they are absent in the Raman spectrum of the undoped sample. The $A_1(\text{LO})$ Raman mode, supposedly located at 577 cm^{-1} [123], was hardly observable because it overlaps with the tail of the intense Si peak. The ratio of the N-related 580 cm^{-1} mode to the ZnO $E_2(\text{high})$ is comparable to that obtained from N-doped ZnO films deposited via rf magnetron sputtering [124].

5.2.5 CL properties

Figure 5.5 shows the CL spectra of undoped and N-doped ZnO nanowires at 80 K. The CL spectra are plotted in a logarithmic scale to improve the ease of interpreting the emission features with low intensities. The spectra of the nanowires are similar to those obtained via CL on the ZnO crystal [125], and consist of a NBE emission at 3.35 eV, which is dominated by donor bound excitons (BX) [56]. Free exciton (FX) emission is strongly suppressed due to the strong near bandgap self-absorption, while both first- and second-order longitudinal optical phonon replicas (FX-LO and FX-2LO) are clearly identifiable in the undoped ZnO nanowires. Their energy separation is approximately 70 meV, which is consistent with the previously measured value for

bulk ZnO [126]. The presence of the phonon replica is a good indicator of the high crystal quality of ZnO nanowires. The DAP emission at 3.24 eV is present in the CL spectra of N-doped nanowires. There is an overlap of the FX-2LO and N-related DAP peaks, as they occur essentially in the same spectral region. According to the CL measurements performed at temperatures down to 15 K, the BX and its phonon replica emissions are enhanced due to the localisation of excitons with the decreasing temperature. Consequently the FX phonon replicas gradually decrease in intensity as the BX channel has a significantly higher recombination efficiency. The background

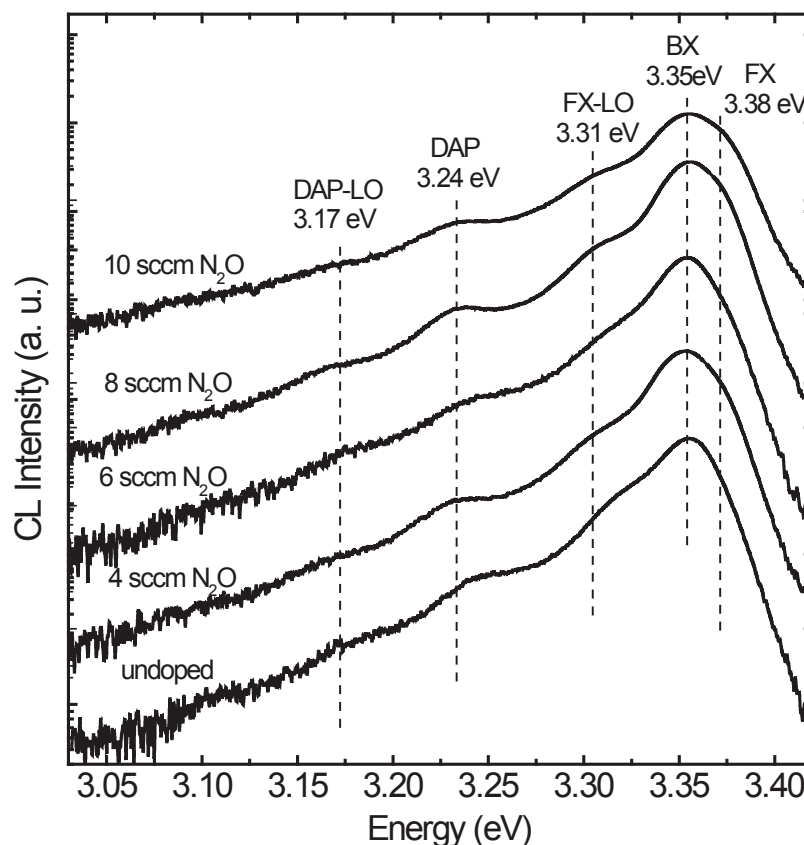


Figure 5.5. CL spectra of undoped and N-doped ZnO nanowires at 80 K. Bound excitons (BX) at 3.35 eV dominate the spectra, and phonon replicas of free exciton (FX) emission are clearly identifiable. DAP bands at 3.24 eV occur in the spectra of N-doped ZnO nanowires. The DAP emission is at the similar spectral region to the second-order phonon replica FX-2LO.

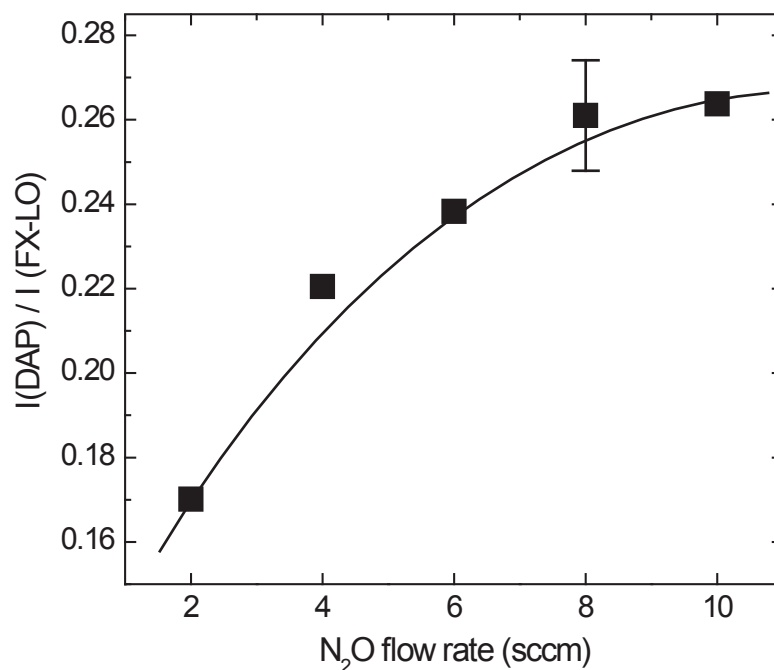


Figure 5.6. Intensity ratio of the DAP emission to the FX-LO peak in N-doped ZnO nanowires as a function of N₂O gas flow rate. The error bars represent one standard error of the mean for 100 CL spectra. The strong correlation of the 3.24 eV intensity with N₂O flow rate indicates that the DAP emission, caused by incorporated N in nanowires, contributes substantially to this spectral region.

phonon replica emissions exert similar interference on the DAP region at 15 K. Assignment of the 3.24 eV emission band to donor-acceptor pair recombination was supported by analysing the intensity ratio of the DAP emission to the FX-LO peaks. Figure 5.6 shows the dependence of $I(\text{DAP})/I(\text{FX-LO})$ ratio on the N₂O flow rate, which shows that the ratio increases with the N₂O content and reaches a maximum at 8 sccm. The DAP emission intensity is directly proportional to the amount of introduced N₂O dopant gas, which indicates that the nitrogen acceptors contribute substantially to this emission and more nitrogen acceptors are created in ZnO nanowires with more N₂O used as the doping source. The present nitrogen acceptors reach a

doping threshold at 8 sccm, which indicates the relatively low nitrogen solubility via the pure *in-situ* N₂O gas flow during the ZnO nanowire growth. The relative intensities of phonon replica bands can be described by a Poisson distribution [127]:

$$I_n = I_{\text{ZPL}} \frac{S^n}{n!} \quad (5.1)$$

Where I_n is the intensity of the n -th phonon replica, I_{ZPL} is the intensity of the zero-phonon line, and S is the Huang-Rhys factor. Using the above relationship, the intensity ratio $\eta = I(3.24 \text{ eV})/I(\text{FX-LO})$ is therefore $S/2$. For the undoped nanowires, $\eta = 0.16$, yielding the Huang-Rhys factor $S = 0.32$, which is entirely consistent with the reported value in ZnO nanowires with comparable diameters [128]. This S value is lower than the reported range of 0.35 — 0.85 for bulk ZnO [45]; however, it is likely due to poorer crystallinity and finite phonon correlation in the nanowires. The intensity ratio η was found to be insensitive to effects of higher excitation density as the e-beam current was varied in the range of 1 — 50 nA, indicating that exciton-exciton interaction or electric fields due to charge trapping do not have a significant effect on the nanowires. There is a possible source of error related to inhomogeneous luminescence in ZnO nanowires, as reported previously [83]. The error bars in Figure 5.6 represent the standard error of the mean, calculated from 100 spectra obtained at different positions on the substrate. Taking this error into account, the trend still conservatively gives an increase of 30% in the intensity ratio. In the CL spectrum of the undoped ZnO nanowires, the FX-2LO is the sole contributor to the 3.24 eV spectral region; while the enhancement of the 3.24 eV CL peak with increasing nitrogen content can be ascribed to the N incorporation in nanowires, which, in later sections, is found to be the donor-acceptor pair emission involving nitrogen acceptors and omnipresent shallow donors.

5.3 Nitrogen doping by plasma annealing

5.3.1 Post-growth doping of nanowires

Compared with the nitrogen doping using unionised sources — *in-situ* introduction of the dopant gases, such as N_2O [46] and NH_3 [129], or through the annealing of ZnO samples in the N-containing gases [130], doping ZnO using the ionised nitrogen source has great advantage [131]. Ionised nitrogen species are more reactive and are more likely to behave as acceptors in ZnO by forming chemical bonds with the surrounding crystal matrix [132]. A traditional nitrogen ion implantation is equipped with a DC ion gun, which uses a high accelerating voltage up to 185 keV [133]. While a radio-frequency plasma device with a relatively low nitrogen ionisation rate (4% N^+ compared to 96% N_2^+) [134] provides a rare-harm atomic nitrogen ion source [135]. Therefore, by using a high frequency rf plasma source, highly ionised nitrogen dopant source can be generated in the plasma chamber with the application of a relatively low voltage (230 V) and low ionisation power (20 W). The ZnO nanowires are heated to 300°C to thermally activate the crystal lattice before the plasma is turned on so that ionised nitrogen can be more readily incorporated.

5.3.2 Structural properties of ZnO nanowires doped by rf N_2 plasma

Figure 5.7 displays the N-doped ZnO nanowires which were grown on silicon (a) and sapphire (b) substrates. ZnO nanowires exhibit vertical alignment with hexagonal tip-facets which indicates the nanowire growth direction is along the *c*-axis of the wurtzite crystal structure. The nanowires have a diameter ranging from 80 to 180 nm and a typical length of 0.6 μm . No changes in the nanowire morphology were detected after the plasma annealing. Compared with the high voltage N implantation [136], which

was normally used for implanting higher dimensional ZnO materials, the rf plasma delivers to the sample an energy several orders of magnitude lower than high voltage N implantation. Assisted by the radio-frequency source, nitrogen dopants can be effectively incorporated into ZnO nanowires at a much lower energy with ~ 230 V cathode bias applied, thus reducing the damage caused to the ZnO nanowire crystal lattice. Although visible structural damage has been observed on the N-implanted ZnO nanowires using an ion accelerating energy up to hundreds of keV [137], the voltage used for a rf plasma source is low enough not to cause morphology change. Figure 5.8 presents the XRD diffraction spectra of the as-grown and N-doped ZnO nanowires by post-growth nitrogen plasma treatment. As shown in Figure 5.8(a), the strong (0002) diffraction indicates that the nanowires are single-crystal nanostructures growing preferentially along the c -axis. Figure 5.8(b) shows that the (0002) peak is broadened after nitrogen plasma treatment while its peak position keeps constant, suggesting a nonuniform lattice distortion in the c -direction. The inset of Figure 5.8(b) shows the (11 $\bar{2}$ 0) peak before and after nitrogen plasma treatment, the blue and pink curves represent the smoothed XRD spectra of N-doped ZnO nanowires and the undoped

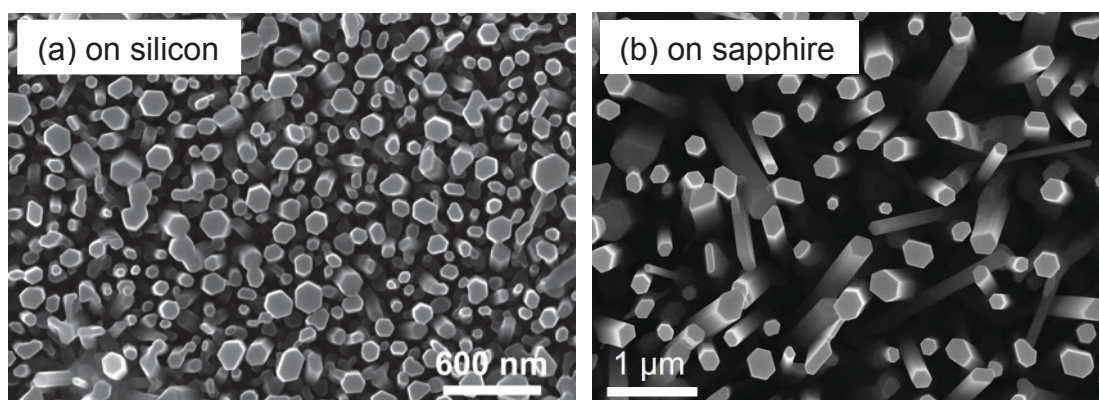


Figure 5.7. SEM images of N-doped ZnO nanowires grown on silicon and sapphire substrates. The nanowires exhibit vertical alignment with hexagonal facets at the tip and no change in morphology is observable after the N₂ plasma treatment.

reference sample, respectively.

The $(10\bar{1}0)$ XRD peak of the N-doped ZnO nanowires exhibits 0.019° shift to higher degrees compared to the as-grown sample, while the $(11\bar{2}0)$ peak in the XRD spectrum

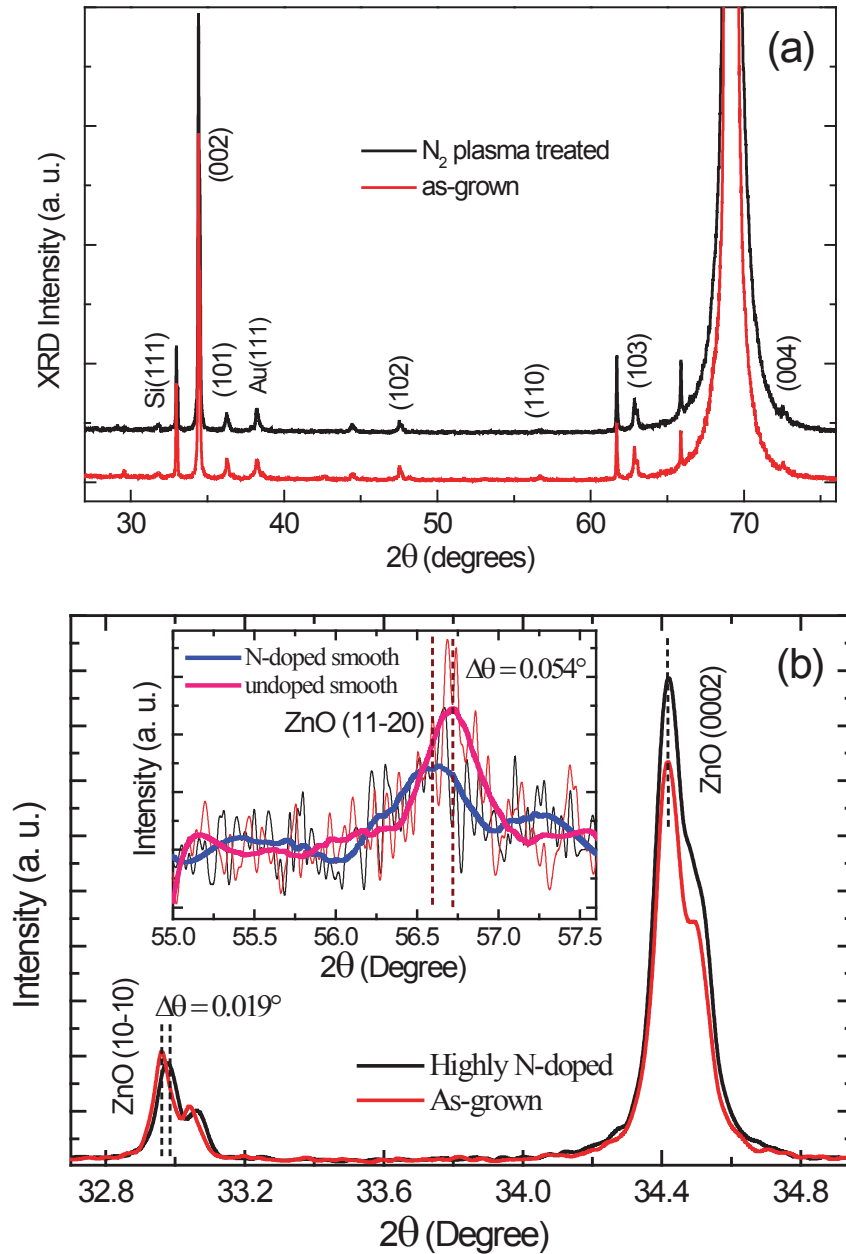


Figure 5.8. XRD patterns of as-grown and N plasma treated ZnO nanowires. (a) displays the wide range XRD spectra. (b): the right shift of the $(10\bar{1}0)$ peak indicates the compressive strain along the m -direction, while the left shift of the $(11\bar{2}0)$ peak suggests the tensile strain along the a -direction.

of the N-doped nanowires shows left shift of $\Delta\theta = 0.054^\circ$, indicating that nitrogen incorporation causes the compressive strain along the m -direction while tensile strain along the a -direction [138]. The strain distribution caused by intense nitrogen plasma in ZnO nanowires indicates that the loosely bound molecular nitrogen N-N aligns perpendicular to the a -direction of the wurtzite lattice structure, which is consistent to the nitrogen alignment model in ZnO developed by Nickel and Gluba [139].

5.3.3 Chemical states of nitrogen in ZnO

Nitrogen species in ZnO can form chemical bonds with the surrounding lattice as well as the impurities present in the material. Electron binding energy at the N 1s core level varies with the formation of different chemical bonds. N 1s XPS peak assignments are: binding energies of 396.5, 398.3, 399.5 and 403.5 eV are assigned to N_o-Zn, N-C, N-H and N-N chemical bonds, respectively [140]. Besides the N-related chemical bonds, molecular (N₂)_o and atomic (N)_o nitrogen species have also been identified in the XPS spectra of N-doped ZnO with binding energies of 396.1 and 404.3 eV [141]. Selection of an appropriate data fitting methodology plays an important role in analysing the XANES spectra for obtaining the accurate ratio of nitrogen species. Different distribution functions have been adopted for fitting the XANES spectra. Lorentzian, Gaussian and Voigt distribution functions were used for fitting the N K -edge X-ray absorption spectra [142].

Figure 5.9 shows the XPS survey scan spectrum of N-doped ZnO nanowires using an excitation X-ray source with a photon energy of 1486.7 eV. The XPS features of zinc and oxygen related peaks are clearly identifiable in the spectrum, which indicates the high crystal quality of the N-doped ZnO nanowires. Zn 3d, Zn 3p_{3/2}, Zn 3s, O 1s, Zn

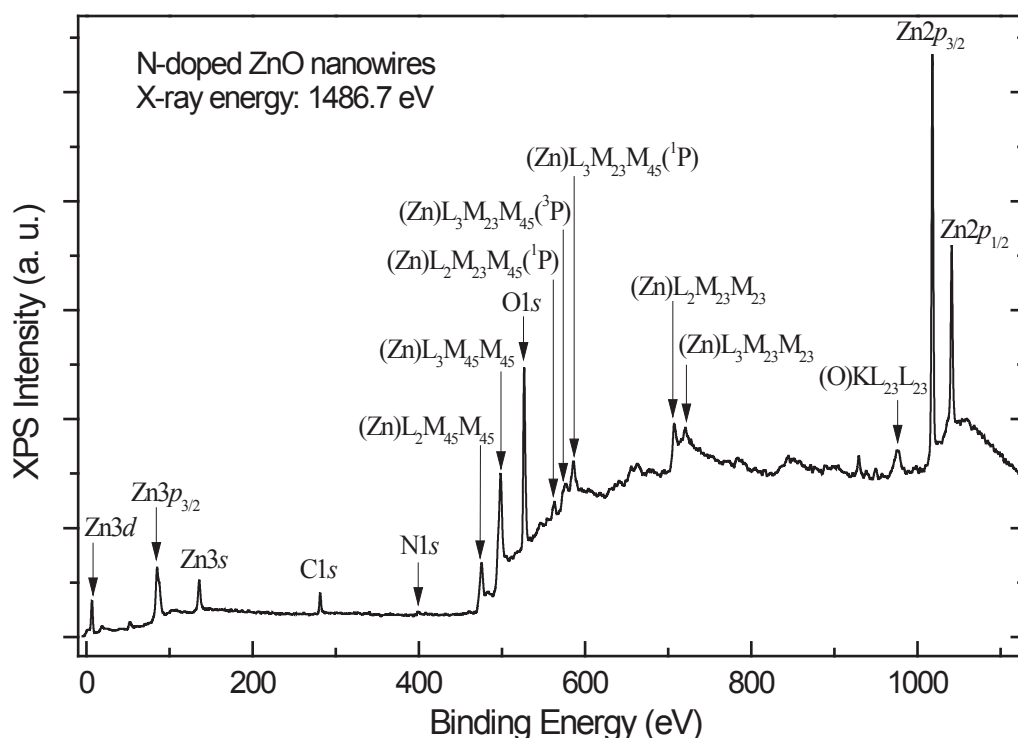


Figure 5.9. XPS survey scan of the N-doped ZnO nanowires. The incident X-ray was set as 1486.7 eV. Zinc, oxygen and carbon are detected in the spectrum. Nitrogen concentration is below the detection limit of the XPS technique [143].

$2p_{3/2}$ and Zn $2p_{1/2}$ are shown at binding energies of 6 eV, 86 eV, 136 eV, 529 eV, 1019 eV and 1039 eV, respectively. N 1s at ~400 eV is not detectable, suggesting that the amount of the nitrogen dopant in the nanowires is below the detection limit of XPS. C 1s XPS peak is observed at 281 eV, which could be originated from the graphite used in the growth or contamination. Only low intensity Auger Zn *LMM* and O *KLL* peaks are detected from the sample.

Figure 5.10 shows the representative nitrogen *K*-edge XANES spectra of the N-doped ZnO nanowires as well as one spectrum from the as-grown sample for comparison. The XANES spectra of N-doped nanowires could be deconvoluted into three Lorentzian peaks to represent resonant electron transitions from the N 1s initial state to the final

unoccupied N-related state of p -symmetry [60], after subtracting an arctangent step function that represents the transition of ejected photoelectrons to the continuum [144].

The components centred at 400.0, 400.7 and 404.5 eV correspond to three chemical

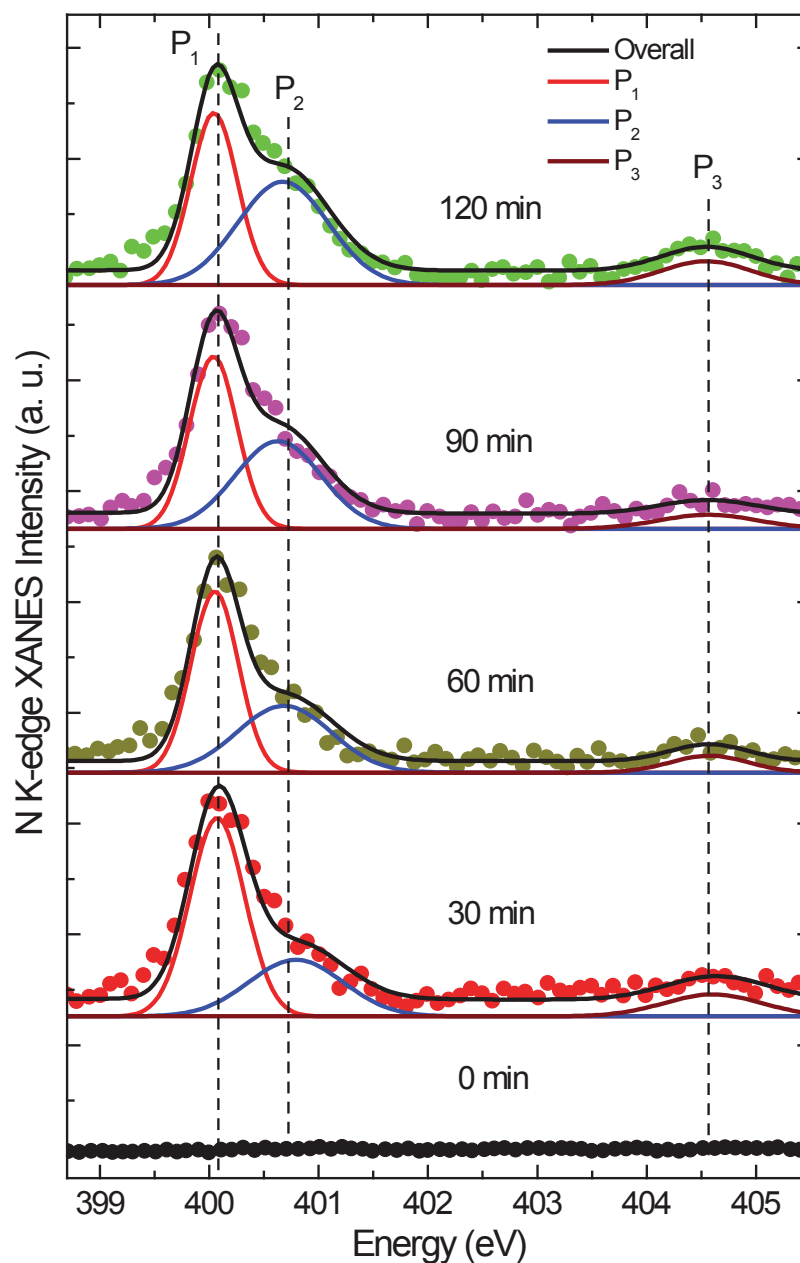


Figure 5.10. XANES spectra of the ZnO nanowires that were plasma annealed for different periods of time. The spectra of the N-doped samples could be fitted to three Lorentzian functions (labelled P_1 , P_2 and P_3), which are associated with three N-related defects N_O , loosely bound N_2 and N_{Zn} , respectively.

states of nitrogen, which are labelled as P_1 , P_2 and P_3 , respectively. The strong resonant peak P_1 at 400.0 eV is at the same resonant position as previously observed in N-doped ZnO crystals [145] and has been assigned to the characteristic $1s$ to $2p\pi^*$ transition in the hybridised N-Zn orbital [146]. The P_2 peak at 400.7 eV is associated with the N $1s$ to π^* transition in the N-N species [147], which is a signature of molecular nitrogen.

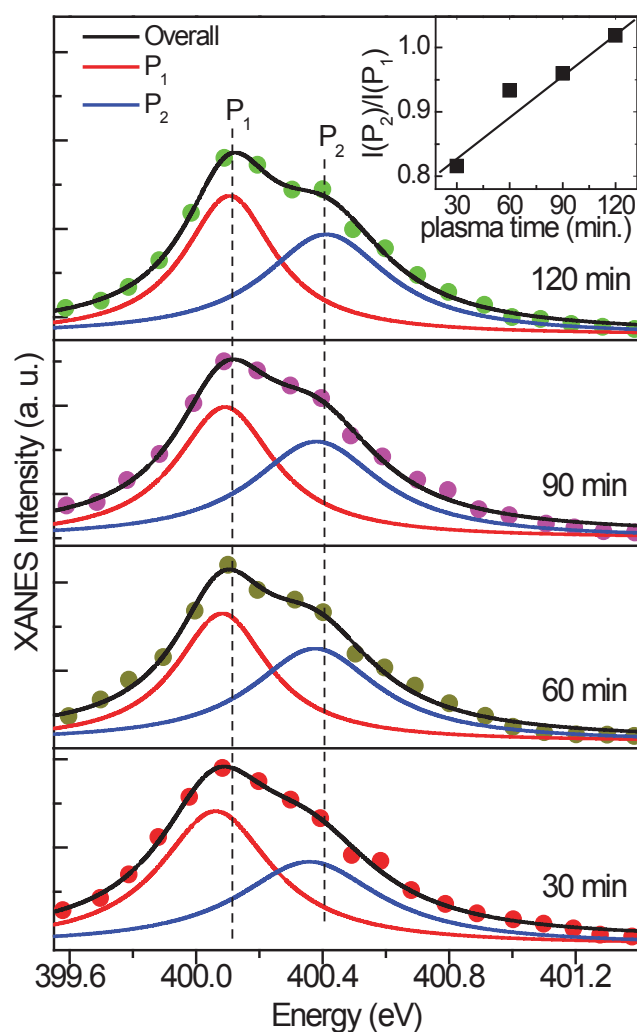


Figure 5.11. N K -edge XANES spectra of N-doped ZnO nanowires after N_2 annealing at 350°C for 30 min. The black squares, red circles, blue rectangles and green diamonds represent the spectra of ZnO nanowires with a rf N_2 plasma time of 120 min, 90 min, 60 min and 30 min, respectively. Each spectrum can be deconvoluted using Gaussian fitting into P_1 component at 400.0 eV and P_2 component at 400.4 eV.

The energy and width of this resonance peak are very similar to the vibration structure of trapped N_2 previously observed in oxides and nitrides, such as ZnO [145], GaN [148] and InN [149], implanted with N ions. As a parameter accurately indicating the bonding arrangement of a dopant in the lattice, the subtle variation of the P_2 peak in the XANES spectra among the compounds confirms that this N_2 species interacts weakly with the surrounding host lattice. The energy of the broad P_3 peak is similar to that of the characteristic absorption peak of N_2O and has been attributed to the N $1s$ to $2p\sigma^*$ transition in N-O species [146]. Accordingly, P_3 is ascribed to N at Zn sites. The P_2 component is enhanced significantly with increasing plasma time, indicating more nitrogen is present as molecular species.

The N K-edge XANES spectra can be deconvoluted into P_1 and P_2 component, while the P_3 peak at 404.5 eV disappears after being annealed in nitrogen gas. P_2 component becomes more pronounced and gradually separates from the P_1 component with the plasma treatment time increasing from 30 min to 120 min, as shown in Figure 5.11. The P_2 intensity increases more slowly in the N-doped ZnO nanowires after N_2 annealing than the solely N plasma treated ZnO nanowires, indicating that the atomic nitrogen is more easily affected by the post annealing after the N doping by plasma.

5.3.4 Luminescence properties

5.3.4.1 Power density-resolved CL of N-doped ZnO nanowires

Figure 5.12(a) shows the CL spectra (10 kV, 0.52 nA) of the as-grown ZnO nanowires, while Figure 5.12(b) shows the CL spectra of the N-doped sample. The CL spectrum of the as-grown nanowires consists of a D^0X emission at 3.355 eV and phonon replicas of free excitons (FX-LO, FX-2LO and FX-3LO) at 3.17, 3.24 and 3.31 eV, respectively.

The absence of the zero phonon FX emission is due to efficient photon self-absorption, while the transmission of the sub-bandgap FX-*n*LO signals is relatively unaffected. Upon plasma annealing, the intensities of the 3.24 and 3.31 eV peaks increase considerably relative to the D⁰X. The enhancement of the 3.31 eV peak after prolonged plasma annealing is attributable to excitons bound to structural defects (*Y* lines), which occurs at the same spectral region as the FX-LO [127].

To gain a better understanding of the 3.24 eV peak behaviour, CL measurements were carried out on both undoped and N-doped ZnO nanowires with the excitation power density increasing from 0.027 to 6.4 W/cm². During the experiment, the power density adjustment was achieved by raising the beam current from 0.03 to 0.52 nA. No shifts in the peak positions were detectable for D⁰X and FX-1LO emissions, whereas the DAP peak of the N-doped nanowires exhibits a perceptible blueshift of about 10 meV. The FX-2LO peak of the undoped nanowires shows no blueshift with increasing beam current, as displayed in Figure 5.12(a). The blueshift is characteristic of a DAP transition and indicates a substantial contribution of the N-related emission to the 3.24 eV peak. Taking into account the Coulombic interaction between closely located donors and acceptors, the photon energy of the DAP recombination can be expressed as [150]:

$$h\nu_{\text{DAP}} = E_g - E_D - E_A + \frac{e^2}{4\pi\epsilon r_{\text{DA}}} \quad (5.2)$$

where E_g is the bandgap energy, while E_D and E_A denote the binding energies of donors and acceptors, respectively. ϵ and e are the usual quantities and r_{DA} is the average donor-acceptor distance. The blueshift of a DAP transition originates from a redistribution from distant donor-acceptor pairs with small Coulomb interaction to

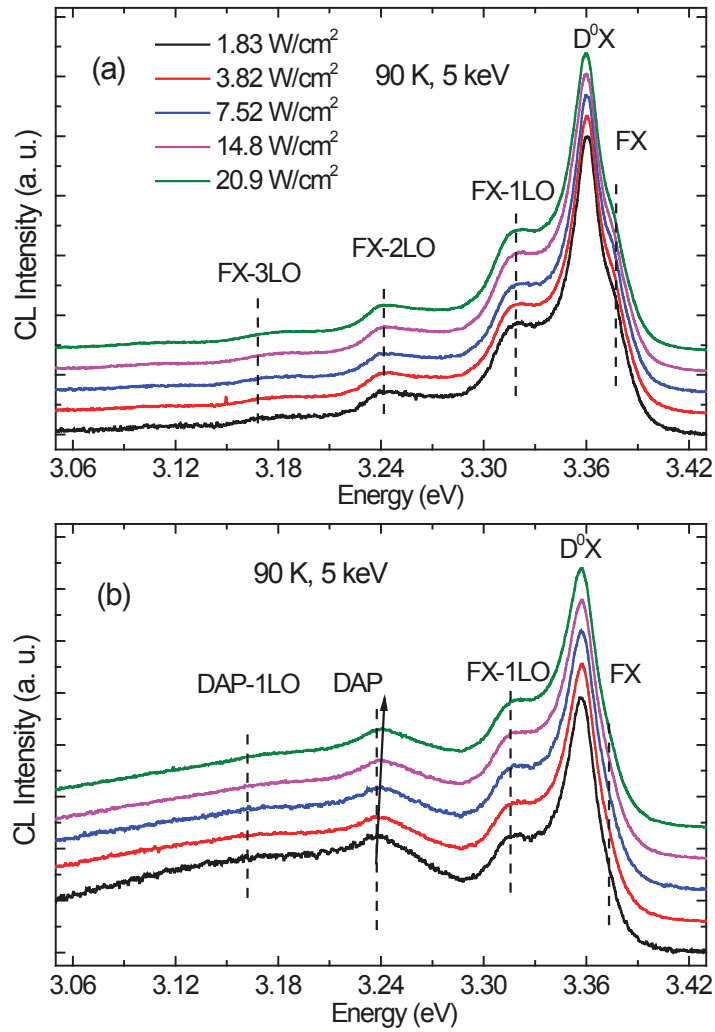


Figure 5.12. Power density-resolved CL spectra of ZnO nanowires. (a) The as-grown nanowires; (b) the N plasma treated ZnO nanowires. The DAP shows clear blue shift with increasing the power of the electron beam.

closer pairs with larger Coulomb energy term as more distant pairs saturate at a faster rate than their closer pairs with increasing excitation. An increase in the beam current above 0.52 nA did not lead to a further blue shift, due to finite numbers of donors and acceptors in the nanowires.

Power density-resolved CL measurements have also been performed on N-doped ZnO nanowires at temperature down to 10 K and the collected spectra are plotted in

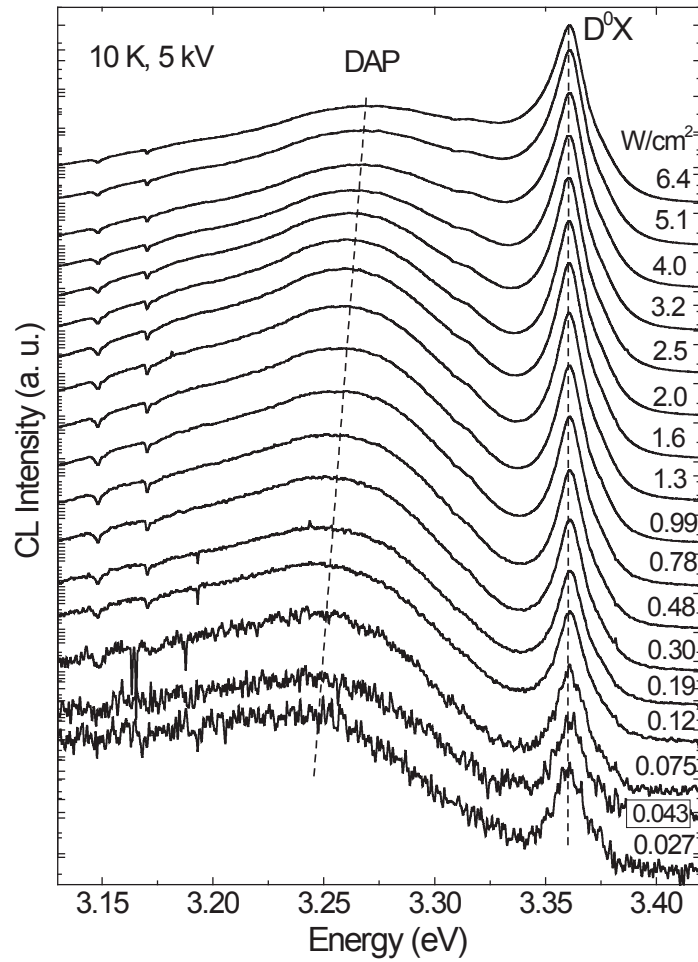


Figure 5.13. Power density-resolved CL spectra of N-doped ZnO nanowires at 10 K. The DAP shows clearer blue shift with the increase of the electron beam power at 10 K compared with the measurements carried out at 90 K.

Figure 5.13. No free exciton (F_{AX}) emission is displayed in the figure due to the strong near-bandgap self-absorption at 10 K. Two distinctive peaks were detected in the near-band-edge emission region — neutral donor bound exciton (D^0X) and the DAP recombination. The D^0X shows a sharp emission in the CL spectra and exhibits no peak shift with increasing power density due to the abundance of the intrinsic shallow donors. The DAP recombination peak occur at 3.25 eV, slightly higher than the DAP peak position in the CL spectra collected at 85 K due to increased band gap at a temperature down to 10 K. The DAP emission shows clear blueshift under the enhanced electron

beam with its peak position shifting from 3.25 eV at an e-beam power density of 0.03 W/cm^2 to 3.27 eV at 6.4 W/cm^2 . The density of donors and acceptors in the sample increases with the power of the electron beam, resulting in shortened donor-acceptor distance.

According to Equation (5.2), the DAP photon energy $h\nu_{\text{DA}}$ will increase with the reduction of the distance between donors and acceptors, r_{DA} . The DAP recombination was eventually saturated with increasing the power of the electron beam due to limited amount of acceptors in the nanowire. As a result, the D^0X to DAP intensity ratio increases with the beam power. In the CL spectra of N-doped ZnO nanowires, a broad background emission was also observed under the DAP peak, which could be due to the defects created by rf nitrogen plasma treatment [151].

Figure 5.14 shows the dependence of the intensity on the electron beam current (I_{B}).

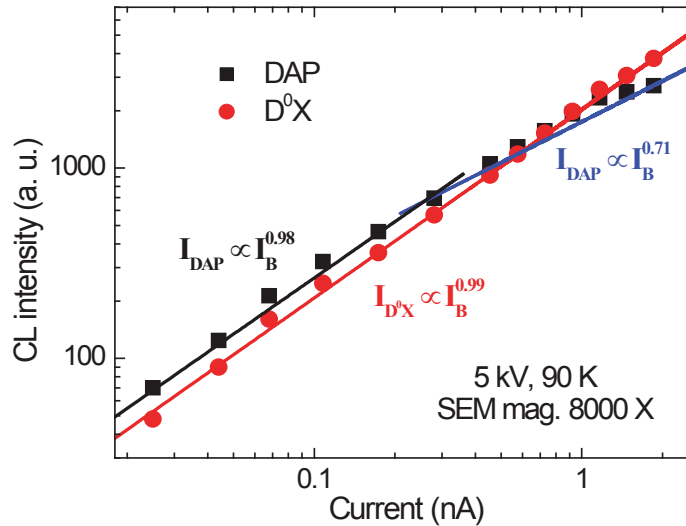


Figure 5.14. Log-log plot of DAP and D^0X peak intensities extracted from the CL spectra of nitrogen plasma-treated ZnO nanowires. Power law fits using straight lines show different dependencies of I_{DAP} and $I_{\text{D}^0\text{X}}$ on I_{B} : $I_{\text{DAP}} \propto I_{\text{B}}^{0.98}$, $I_{\text{DAP}} \propto I_{\text{B}}^{0.71}$ and $I_{\text{D}^0\text{X}} \propto I_{\text{B}}^{0.99}$, which are represented by the black, blue and red lines, respectively.

The intensities of the luminescence were collected at different currents with all other parameters identical. The logarithmic axes were used for figure plotting and the data points were fitted using a linear equation. Both the D⁰X and the DAP emissions are enhanced with increasing the electron beam current, but their variations follow different trends. D⁰X dots can be fitted into a straight line using a power-law exponent of 0.99 with its intensity dependence expressed as: $I_{D^0X} \propto I_B^{0.99}$. Compared with the D⁰X emission, the DAP emission intensity does not show closely linear increase with the electron beam current due to the limited donor-acceptor pairs existing in ZnO nanowires. At electron beam currents below 0.3 nA, the intensities of the ZnO DAP emission can be fitted into $I_{DAP} \propto I_B^{0.98}$ with the power-law exponent being 0.98; while above 0.3 nA, the relationship has a different form: $I_{DAP} \propto I_B^{0.71}$. The D⁰X peak intensity exhibits linear increase with the electron beam current, while the intensity of the DAP peak increases slower at current above 0.3 nA and finally approaches saturation when I_B reaches 2 nA.

According to the excitation-power dependencies, the DAP intensity exhibits slower increase at e-beam currents higher than 0.3 nA in comparison with the D⁰X due to saturation effects. The intensities of DAP and D⁰X emissions follow similar trends in the low current region with the power-law fitting exponents being 0.98 and 0.99, respectively. However, the DAP quickly saturates as the current increases to above 1 nA, indicating that the electron beam current threshold for the DAP saturation is around 1 nA. In the low electron current region, there are sufficient donors and acceptors contributing to the emission; while at high e-beam currents, due to the small number of incorporated nitrogen acceptors, limited donor-to-acceptor transition channels in the bandgap will soon be occupied, leaving only donor states.

5.3.4.2 Characteristics of N-doped ZnO emissions

Figure 5.15 displays the representative CL spectra of as-grown and N-doped nanowires at various temperatures between 15 and 160 K, together with the assignments of the spectral features. All the spectra were displayed in the logarithmic scale to emphasise the DAP emission peak and high-order longitudinal optical (LO) phonon replicas with low intensities. As shown in Figure 5.15(a), the first- and second-order phonon replicas of free exciton emission (FX-LO and FX-2LO) are separated by the commonly observed optical phonon energy $E_{LO} = 72$ meV; while at 15 K the energy separation between FX-LO and DAP in N-doped nanowires is 77 meV [Figure 5.15(b)]. The

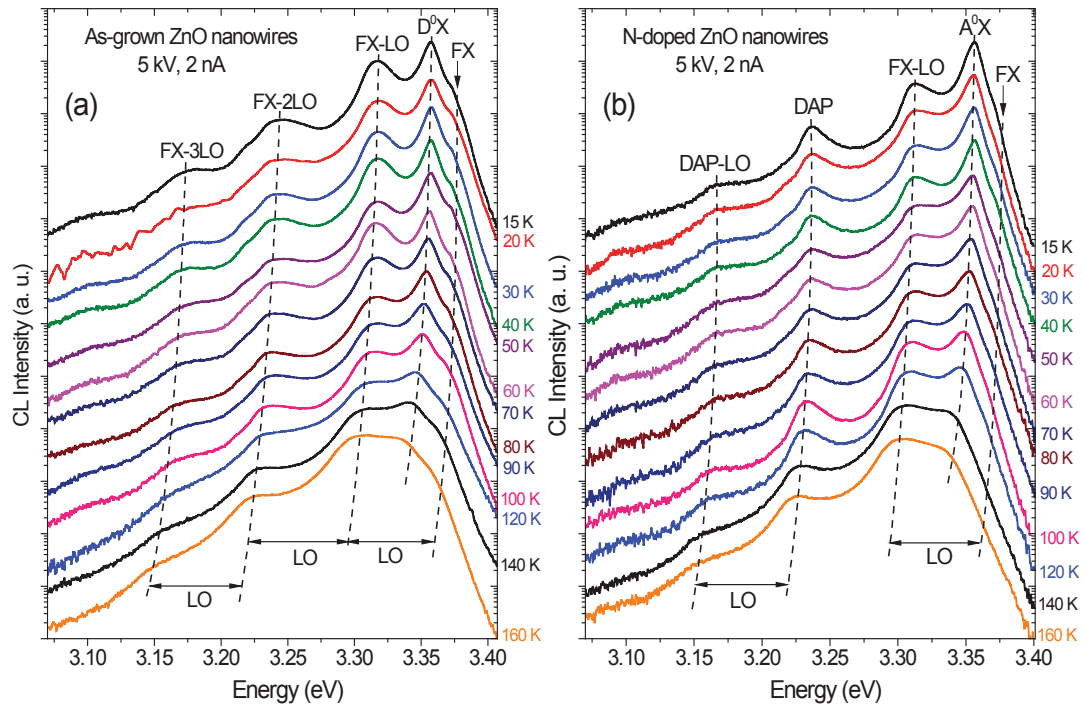


Figure 5.15. Temperature-resolved CL spectra of as-grown and N-doped ZnO nanowires ($E_B = 5$ keV, $I_B = 2$ nA). The CL intensity is plotted in a logarithmic scale and the spectra are vertically shifted for clarity. The dashed curves indicate the peak positions of D^0X , A^0X , phonon replicas of FX and DAP. The separation of N-related DAP and FX-LO is 77 meV, significantly greater than the energy of longitudinal optical phonons (72 meV).

transition energies of FX-LO, FX-2LO and DAP obtained from the CL spectra are plotted in Figure 5.16 as a function of temperature. The temperature dependencies of FX-LO and FX-2LO are adequately described by the standard equations [126], which are displayed beside each data set in Figure 5.16. Due to the thermal energy $\frac{1}{2}k_B T$ contribution, the FX-2LO and N-related DAP occur essentially at the same energy above 140 K, but gradually separate with the temperature decrease. Because the donor

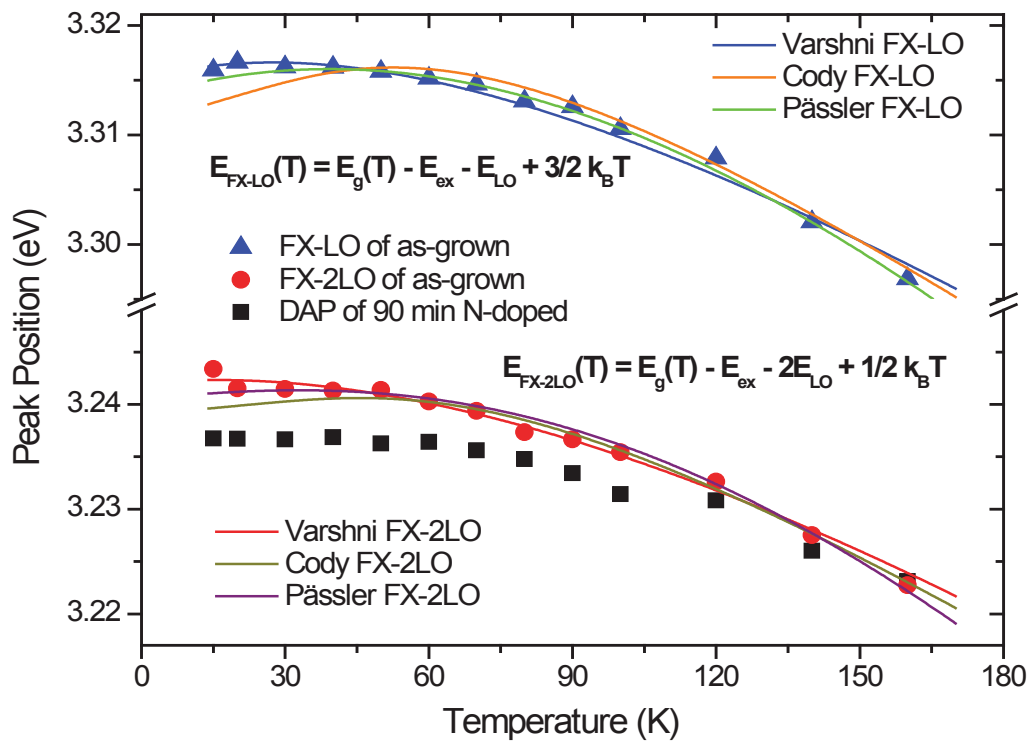


Figure 5.16. Temperature dependences of FX-LO, FX-2LO and N-doped DAP transition energies obtained from the CL spectra. The experimental data are presented by the symbols, whereas the solid lines are simulated curves based on the equations shown in the figure. The binding energy of free excitons is assumed to be independent of temperature in the range from 15 K to 160 K ($E_{LO} = 72$ meV). $E_g(0) = 3.438$ eV is used as the bandgap energy at 0 K. The other fitting parameters were: $\alpha = 4.6 \times 10^{-4}$ eV/K and $\beta = 230$ K for Varshni's model; $k = 0.090 \pm 0.004$ eV and $\theta = 230 \pm 10$ K for Cody's model; $\alpha = 6.2 \pm 0.4 \times 10^{-4}$ eV/K and $\Theta = 385 \pm 15$ K for Pässler's model [152].

ionisation energy is lower than the ionisation energy of acceptors in N-doped ZnO, shallow donors will be thermally ionised prior to acceptors with the temperature increasing from 5 K, as previously reported by Thonke *et al.* [58]. According to the extracted CL data points, the DAP peak position is almost unchanged due to the conversion of DAP recombination to (e, A) transitions despite the bandgap shrinkage with the temperature increasing from 15 K to 60 K.

To draw a direct comparison between the DAP recombination and FX phonon replicas, the peak positions of DAP, FX-LO and FX-2LO are extracted from the CL spectra collected at temperatures from 15 K to 160 K and the data points are plotted in Figure 5.16. The FX-LO and FX-2LO energies can be fitted into standard temperature-dependent equations [153]:

$$E_{\text{FX-LO}}(T) = E_g(T) - E_{\text{ex}} - E_{\text{LO}} + \frac{3}{2}k_{\text{B}}T \quad (5.3)$$

for the FX-LO, and

$$E_{\text{FX-2LO}}(T) = E_g(T) - E_{\text{ex}} - 2E_{\text{LO}} + \frac{1}{2}k_{\text{B}}T \quad (5.4)$$

for the FX-2LO.

The bandgap, $E_g(T)$, is firstly approximated by using Varshni's formula,

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{(T + \beta)} \quad (5.5)$$

where $E_g(0)$ is the band gap energy at 0 K. α and β are two material-dependent constants.

By fitting the temperature-dependent FX-2LO peak positions of the as-grown ZnO nanowires, α and β are determined as 4×10^{-4} eV/K and 265 K, respectively.

By using the equation proposed by Cody, the bandgap energy $E_g(T)$ can be expressed as [154]:

$$E_g(T) = E_g(0) - \frac{k}{\exp(\theta/T) - 1} \quad (5.6)$$

with fitting parameters $E_g(0) = 3.438$ eV, $k = 0.090 \pm 0.004$ eV, $\theta = 230 \pm 10$ K. θ is related to the Einstein temperature θ_E , which represents the effect of the average phonon interaction in the system and can be determined from the correlation between Einstein temperature and Debye temperature (θ_D): $\theta_E = (3/4) \theta_D$. This model was also referred to as Bose-Einstein model [155], taking into account the Einstein temperature θ_E used for determining the θ value.

A semiconductor bandgap model reported by Pässler, which involves the effect of the electron-phonon interaction, has the form [152]:

$$E_g(T) = E_g(0) - \frac{\alpha\theta}{2} \left[\sqrt[p]{1 + \left(\frac{2T}{\theta}\right)^p} - 1 \right] \quad (5.7)$$

where $E_g(0)$ is the bandgap energy at 0 K, $\alpha = 6.2 \pm 0.4 \times 10^{-4}$ eV/K, $\theta = 385 \pm 15$ K. In this equation, parameter p has form of $p = 1 + \nu$, and ν is the line shape factor which controls the spectral function $f(\varepsilon) \propto \varepsilon^\nu$ in Pässler's bandgap model.

In Figure 5.16, the experimentally measured peak positions FX-LO, FX-2LO of the as-grown ZnO nanowires and the DAP emission of the N-doped sample as a function of temperature are denoted using blue triangles, red circles and black squares, respectively. The blue and red curves are the fittings for FX-LO and FX-2LO of the as-grown ZnO nanowires with the bandgap $E_g(T)$ calculated according to Varshni's equation. The pink and green curves represent the fittings based on the Bose-Einstein model. The fitting

curves using Pässler model were denoted by the green and purple lines for FX-LO and FX-2LO variations.

Varshni's model and Pässler's model fit well at temperatures from 15 K to 160 K, while the fitting curve using Cody's model bends to low energy side when the temperature approaches 15 K. Such deviation off the experimental data by Cody's fitting should be due to the average phonon effect when determining Einstein temperature θ_E in this model. Although the thermal dilation effect is not included in the fitting using Pässler's model, the FX-LO and FX-2LO data points at 15 K — 160 K temperature range still fit into this model. The DAP peak position deviates from the standard FX-2LO equation at temperatures below 160 K. As the temperature decreases from 160 K to 15 K, the gap between DAP and FX-2LO becomes larger, suggesting that the DAP recombination in ZnO nanowires exhibits different dependence on the temperature thus cannot be fitted into exciton phonon replica models.

5.3.4.3 Molecular nitrogen acceptors

Figure 5.17 shows the CL spectra (5 kV, 0.52 nA) of individual ZnO nanowires, recorded from the same samples as in Figure 5.7. The CL spectrum of the as-grown nanowires consists of a D^0X emission at 3.355 eV and phonon replicas of free excitons (FX-LO and FX-2LO) at 3.313 and 3.237 eV, respectively. The absence of the zero phonon FX emission is due to efficient photon self-absorption, while the transmission of the sub-bandgap FX- n LO signals is relatively unaffected. Nitrogen doping produces two significant changes to the CL spectra. Firstly, a 4 meV redshift of D^0X emission at 3.355 eV is observed; this peak at 3.351 eV is ascribed to neutral acceptor bound exciton (A^0X) in N-doped ZnO. Secondly, a new peak at 3.232 eV emerges that is

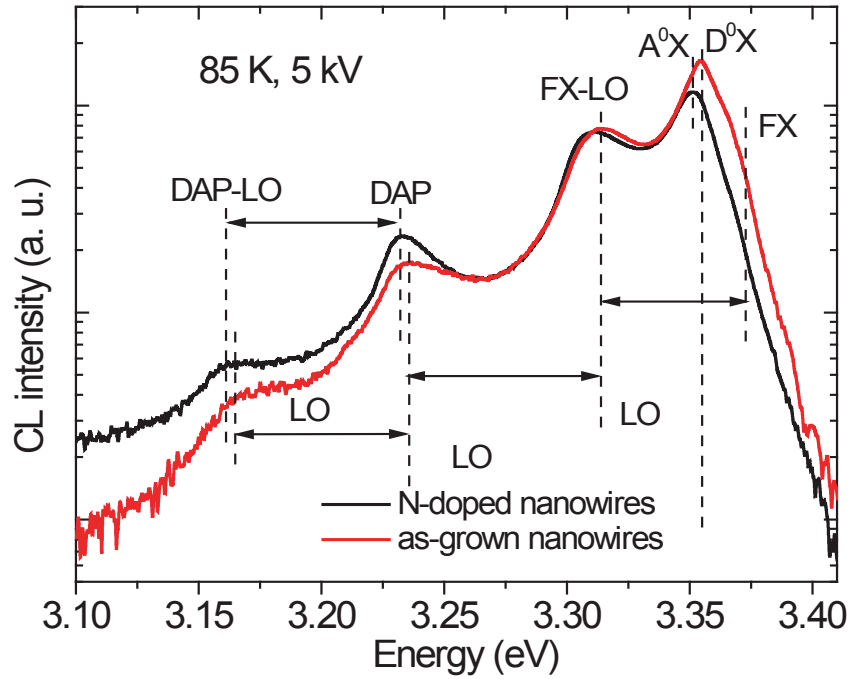


Figure 5.17. CL spectra of as-grown and nitrogen plasma annealed ZnO nanowires. The spectra are displayed in the logarithmic scale to emphasise the CL intensities of phonon replicas. Acceptor-bound exciton emerges in the N-doped sample. The notable enhancement at 3.232 eV is ascribed to N-related DAP emission.

highly overlapped with the FX-2LO, leading to the pronounced decrease in the $I(\text{FX-LO})/I(\text{FX-2LO})$ ratio after N-doping which should be constant at a given temperature. Additionally, the 3.232 eV peak has a Gaussian-like shape following N incorporation, while FX- n LO phonon replicas are highly asymmetric peaks due to the Maxwellian distribution of the free exciton kinetic energies involved in the phonon scattering [156]. Accordingly, this emission is attributed to DAP transition. It is noteworthy that annealing the nanowires in Ar gas does not alter the CL properties of the nanowires.

Further support for this assignment comes from the temperature dependence of FX replica and DAP peak positions (see Figure 5.16 for the temperature-dependent characteristics of DAP and bound exciton peaks). Numerical simulation shows the

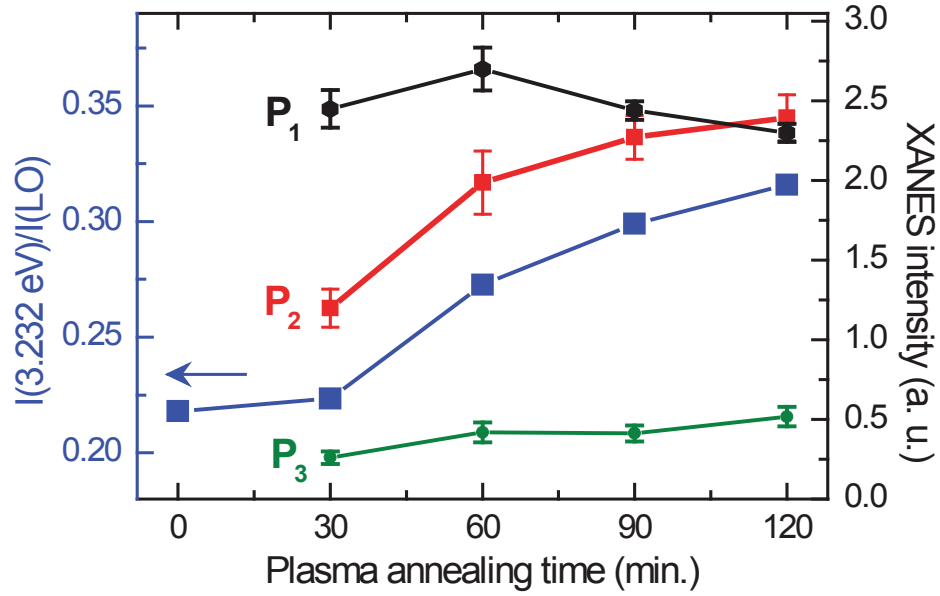


Figure 5.18. Dependence of CL peak intensity ratio $I(3.232 \text{ eV})/I(\text{LO})$ intensity and XANES components P_1 , P_2 and P_3 on plasma annealing time for ZnO nanowires. The direct correlation between the $I(3.232 \text{ eV})$ emission and the P_2 intensity indicates the involvement of N_2 in the DAP emission.

variations of FX-LO and FX-2LO peak positions follow closely the standard equations (presented in Figure 5.16) with a fitting parameter $E_{\text{FX}} = 3.378 \text{ eV}$ (for bulk ZnO, $E_{\text{FX}} = 3.375 \text{ eV}$ [56]). Due to the thermal energy $\frac{1}{2}k_{\text{B}}T$ contribution to $E_{\text{FX-2LO}}$ [157], the FX-2LO and N-related DAP occur essentially at the same energy above 140 K, but gradually separate with decreasing temperature. The DAP transition in N-doped nanowires exhibits a slight blue shift with increasing excitation density (Figure 5.13). In this case a weak blue shift is not unexpected since only a small number of near donor-acceptor pairs exist due to the low concentration of nitrogen acceptors.

Based on the aforementioned phenomena, the identity of the acceptor in the DAP transition can be determined. In the report on ZnO-based LED, Tsukazaki *et al.* [158] reported that a nitrogen concentration of 10^{20} cm^{-3} produced only $10^{16} \text{ holes/cm}^3$ in *p*-

type ZnO films grown by molecular beam epitaxy. Figure 5.18 shows the integrated intensities of the P_1 , P_2 and P_3 components together with the CL $I(3.232\text{ eV})/I(\text{LO})$ peak intensity ratio as a function of plasma time. The difficulty in separating the overlap contributions of DAP and 2LO can be overcome by using the integrated intensity of the 3.232 eV peak; the increase in this peak intensity signifies the intensity of the N-related DAP. The XANES intensities represent the numbers of N_O , loosely bound N_2 and N_Zn in the nanowires. Among the three chemical states of nitrogen in the nanowires, the P_2 centre is the only candidate that can be responsible for the increase in the DAP intensity. The trend of P_1 has no association with the DAP emission, while P_3 can be ruled out since the substitution of N atom, which contains three more valence electrons than Zn, would cause N_Zn or its complex to act as a donor [159]. The increase in the $I(3.232\text{ eV})/I(\text{LO})$ ratio is not exactly proportional to the change of P_2 intensity since the intensities of the signature CL peaks are dependent on the capture cross section and concentration of all radiative and non-radiative recombination centres as well as the excitation conditions due to saturation effects [114]. It is noteworthy that the P_3 donor increases slightly in concentration with plasma time and could act as a compensation centre in N-doped nanowires. The enhancement of the DAP intensity is not associated with the overall nitrogen content, which remains almost unchanged for anneals longer than 30 min. The direct correlation between the P_2 and $I(3.232\text{ eV})$ strongly indicates the involvement of loosely bound N_2 in the DAP transition and supports the N_2 acceptor model [66], in which N_2 at a Zn site is weakly bound to the lattice and retains most of its molecular characteristics. Atomic N at the O site or its complexes have been theoretically predicted to be the shallow acceptor [159]; however, this possibility can be ruled out for ZnO nanowires. While interstitial N_2 is known to readily form in GaN

[148], the presence of such species in a large fraction is not unexpected for ZnO and this could provide a new route for enhanced nitrogen acceptor incorporation. It is significant that the data recorded in the surface sensitive total electron yield (TEY) mode exhibit completely different XANES spectra with abnormally high backgrounds, presumably due to nitrogen-containing contamination on the nanowire surface. The use of the TFY detection mode as a bulk probe guarantees that the detected N_2 is representative of the bulk property of the nanowires. In addition, the self-absorption effects of nitrogen on the TFY data could be avoided because of small diameter of the nanowires.

Under the nitrogen plasma conditions used, ionised atomic and molecular nitrogen species generated in the plasma are accelerated towards the samples. The probability of a N_2^+ disassociating into 2 N atoms depends on the incident energy when the ion strikes a solid surface [160]. The energy required to break the bond between two N atoms in a N_2^+ molecule is about 9 eV [161], thus the disassociation probability is very close to unity in this work. Nitrogen atoms are more readily incorporated into the nanowires than their molecular counterparts and initially incorporated substitutionally at O sites. Given the small nanowire diameters, N atoms will diffuse throughout the entire nanowire volume, whereas gaseous nitrogen adsorbs onto the nanowire surface and then desorbs from the sample by prolonged plasma annealing [66]. As seen in Figure 5.18, prolonged plasma annealing did not lead to a significant increase in the overall nitrogen content but instead changed the relative concentrations of nitrogen species. N_2 is known to have a lower formation energy than N_O [66], and given the ballistic transport of atoms in nanowires at elevated temperatures, the pairing of N atoms is expected. First-principles calculations by Wang and Zunger [162] indicated that N_O is

metastable due to an excess energy in the N bonds to the surrounding Zn atoms, leading to the migration of N from this defect at elevated temperatures and the attraction of a second N atom. The observed plasma time-dependent behaviours of the N_O and loosely bound N_2 species in this work are consistent with this theoretical prediction.

5.3.5 Raman scattering of nitrogen plasma annealed ZnO nanowires

The Raman spectrum of the bare α -plane sapphire substrate (Figure 5.19) shows a dominant peak at 398 cm^{-1} , which was assigned as E_g mode [163]. Sapphire has a much lower Raman scattering cross section than Si, so the ZnO nanowires grown on sapphire substrates are the excellent candidate samples for carrying out Raman spectroscopy measurement. However, sapphire is also significantly less conductive than silicon, which will cause strong charging effects, such as image drift and flashover when

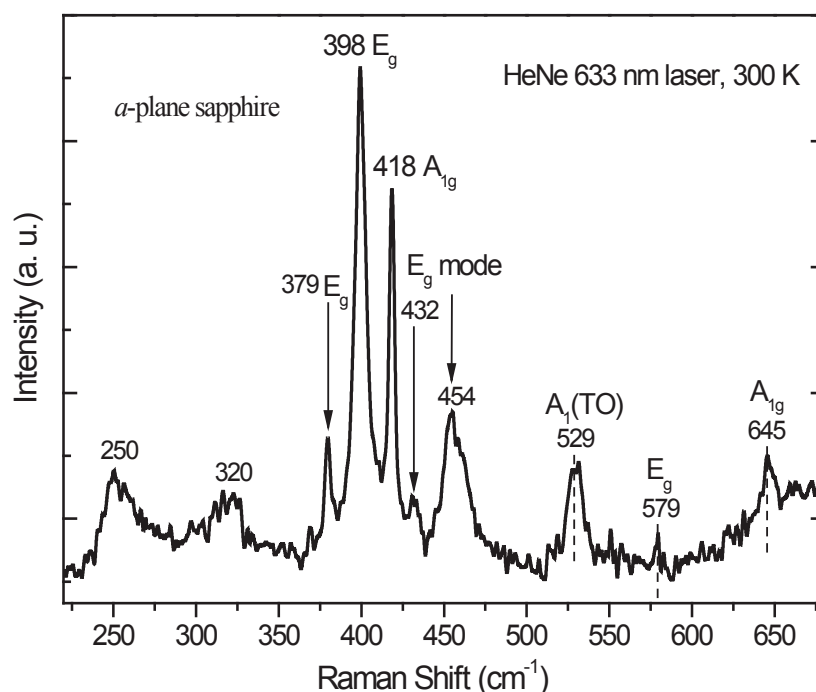


Figure 5.19. Raman spectrum of a bare α -plane sapphire substrate using a He-Ne 633 nm red laser excitation source attached to the Renishaw inVia Raman microscope.

observed in the scanning electron microscope for CL measurements. Spatially resolved CL measurements, e. g., CL mapping, require highly stabilised electron beam scanning of the sample. Consequently Si was the preferred substrate material.

The Raman spectra of ZnO nanowires with different nitrogen plasma treatment times are displayed in Figure 5.20. A prominent change with the nitrogen doping is the enhancement of the Raman mode at $\sim 580\text{ cm}^{-1}$ with the increase of nitrogen plasma treatment time, indicating that this Raman vibration is related to the increased incorporation of ionised nitrogen species. Considering the small diameter of ZnO nanowires, atomic nitrogen species can easily diffuse over the whole nanowire within 30 min. Thus the more pronounced Raman peak at $\sim 580\text{ cm}^{-1}$ with the nitrogen plasma

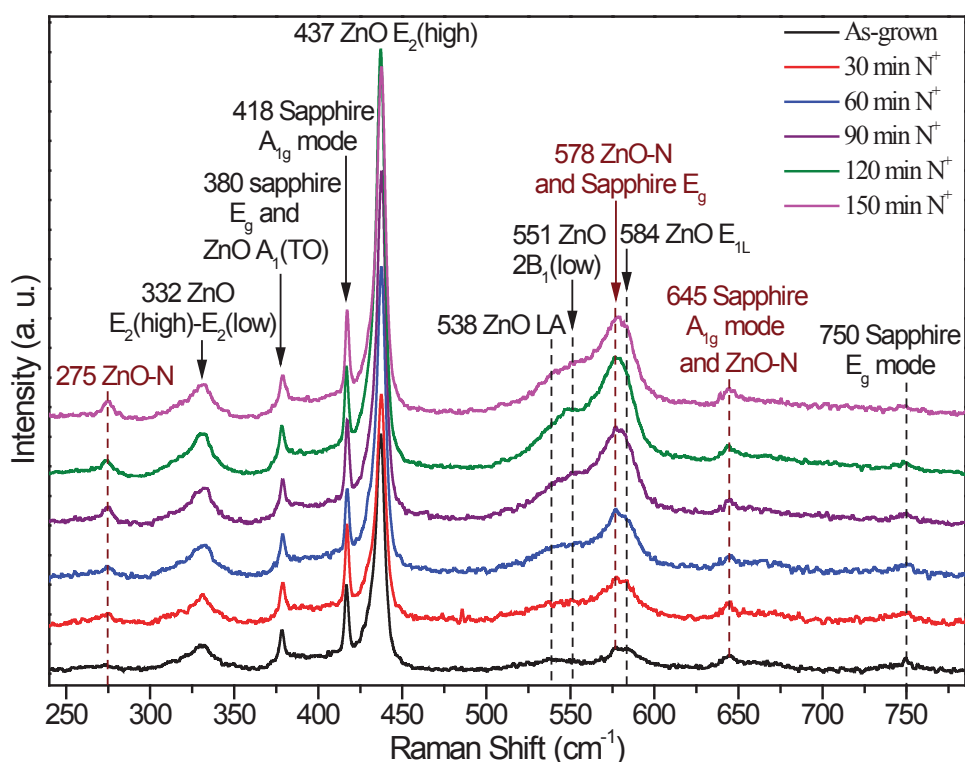


Figure 5.20. Raman spectra of as-grown and N plasma treated ZnO nanowires with nitrogen plasma treatment time increasing from 30 min to 150 min. The N-related Raman peaks emerge after N-doping and are enhanced with the prolonged N plasma time.

time is ascribed to the conversion of atomic nitrogen into molecular nitrogen species rather than the increase of the overall amount of nitrogen.

The Raman peaks at 270 cm^{-1} and 645 cm^{-1} are also observed in the Raman spectrum of the as-grown ZnO nanowires. These two modes do not follow the same trend as the molecular nitrogen mode at 580 cm^{-1} , suggesting that these two Raman modes are not related to the incorporation of atomic nitrogen species. The 645 cm^{-1} mode remains nearly constant among nitrogen plasma treated samples, while the peak at 270 cm^{-1} becomes sharper for the samples treated by N_2 plasma longer than 90 min. Convincing evidence has proven that the anomalous Raman mode at $\sim 274\text{ cm}^{-1}$ is induced by interstitial Zn clusters [120]. During the rf nitrogen plasma treatment, host Zn atoms are knocked into the interstitial sites by the inserted nitrogen ions, so the Raman mode at 270 cm^{-1} could be used as an indicator of the atomic nitrogen incorporated at the Zn vacancy sites (N_{Zn}). The 270 cm^{-1} Raman mode exhibits low intensity throughout the samples of different doping levels, indicating that the N_{Zn} does not exist in ZnO in a large amount, and atomic nitrogen may migrate to the interstitial sites forming loosely bound N-N molecules.

The Raman peaks at 270, 332, 379, 540, 580, 645 and 750 cm^{-1} were fitted using Lorentzian distribution equations and the integrated intensities as a function of the nitrogen plasma time are presented in Figure 5.21. Sapphire Raman modes at 379 cm^{-1} and 750 cm^{-1} are reduced in the N-doped ZnO nanowires with 150 min N plasma time, while the peaks at 275 cm^{-1} and 645 cm^{-1} exhibit Raman scattering intensity similar to other N-doped samples. Although N_o species have low solubility in ZnO under equilibrium conditions [164], this type of nitrogen has a low formation energy in the system and is relatively stable. The comparatively stable and weak Raman scattering at

645 cm^{-1} indicates this mode is induced by the nitrogen at the oxygen vacancy sites, which keeps almost constant throughout ZnO nanowire samples with different amounts of nitrogen plasma treatment time.

Wang *et al.* [165] observed a broadening effect of the 575 cm^{-1} Raman peak with enhanced N^+ implantation, which was attributed to the increased density of phonon states. Friedrich and Nickel [119] also showed that the broadening of the 577 cm^{-1} band to the low-wavenumber side in the Raman spectrum of N^+ -implanted ZnO. However, the additional Raman mode at around 550 cm^{-1} was regarded as a tail of the Raman scattering at $\sim 577 \text{ cm}^{-1}$ and the broadening effect is not fully investigated by far. The additional Raman feature at $\sim 540 \text{ cm}^{-1}$ can be resolved as a single Raman peak, which has been ascribed to disorder-activated silent $2\text{B}_1(\text{low})$ mode and LA overtones along L - M and H lines [166, 167]. The silent $2\text{B}_1(\text{low})$ mode at $\sim 540 \text{ cm}^{-1}$ is barely noticeable in the Raman spectrum of the as-grown ZnO nanowires, while the enhancement of this

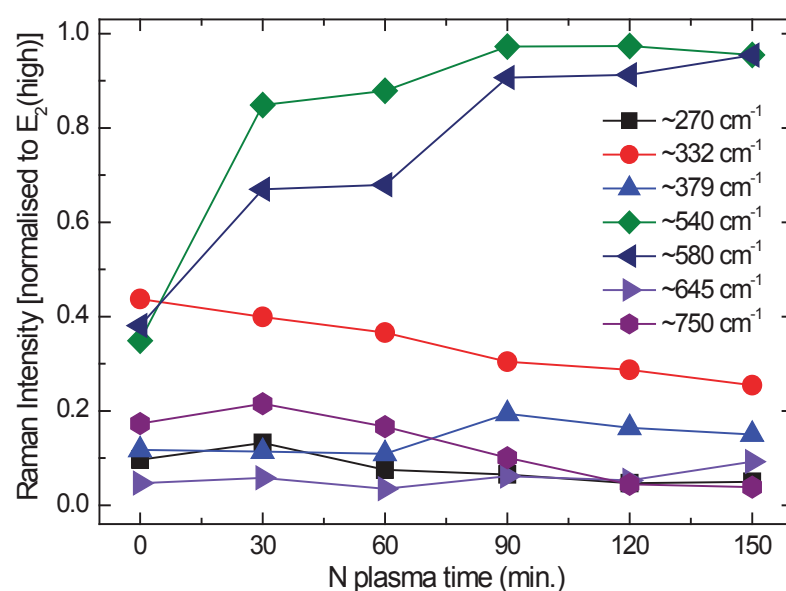


Figure 5.21. Extracted Raman peak intensities versus N plasma time. The Raman intensities are normalised to the dominant $\text{E}_2(\text{high})$ mode of ZnO in each spectrum. N-related Raman peaks are enhanced with the increase of the N_2 plasma time.

peak in the N-doped samples could be due to the activation of the $2B_1(\text{low})$ scattering by nitrogen plasma, or due to the increased density of acoustic phonons by lattice structural damage [119] — for instance, more V_{Zn} sites are created after the N_{Zn} migrates into the interstitial sites forming loose N-N bonds.

The peak at 551 cm^{-1} is enhanced and broadened with increasing the nitrogen plasma treatment time, which is attributable to the enhancement of the second order of the $B_1(\text{low})$ mode at 275 cm^{-1} [166]. As shown in Figure 5.8, nitrogen plasma treatment causes compressive strain along the m -direction and tensile strain along the a -direction, thus breaking the translational symmetry of ZnO lattice. Such structural disorder due to the breakdown of crystal lattice translational symmetry can activate the Raman scattering of the silent modes in ZnO. With the increase of the nitrogen plasma treatment time, a shift of the Raman mode from $\sim 538\text{ cm}^{-1}$ to $\sim 551\text{ cm}^{-1}$ is observed. Such shift can be explained by considering a relatively stable A_1 LA phonon overtone and the enhanced $2B_1(\text{low})$ mode with gradually increased plasma time.

The LA phonon overtone of A_1 symmetry at $\sim 538\text{ cm}^{-1}$ is shown in the Raman spectrum of the as-grown ZnO nanowires and it gradually merges into the $2B_1(\text{low})$ mode with the increase of the nitrogen plasma treatment time, indicating that this mode originates from the intrinsic ZnO lattice structure and that its intensity keeps almost constant with the increase of the incorporated nitrogen dopants. The intensity of the A_1 LA phonon overtone at $\sim 538\text{ cm}^{-1}$ indicates the crystallinity of the ZnO wurtzite lattice structure. The comparatively stable phonon overtones of LA along the L - M and H lines of the Brillouin zone indicates that the ZnO nanowires retained high crystal quality after the nitrogen plasma processing, which is also consistent with the wurtzite crystal structure reflected by the hexagonal top facet in the SEM image (Figure 5.7).

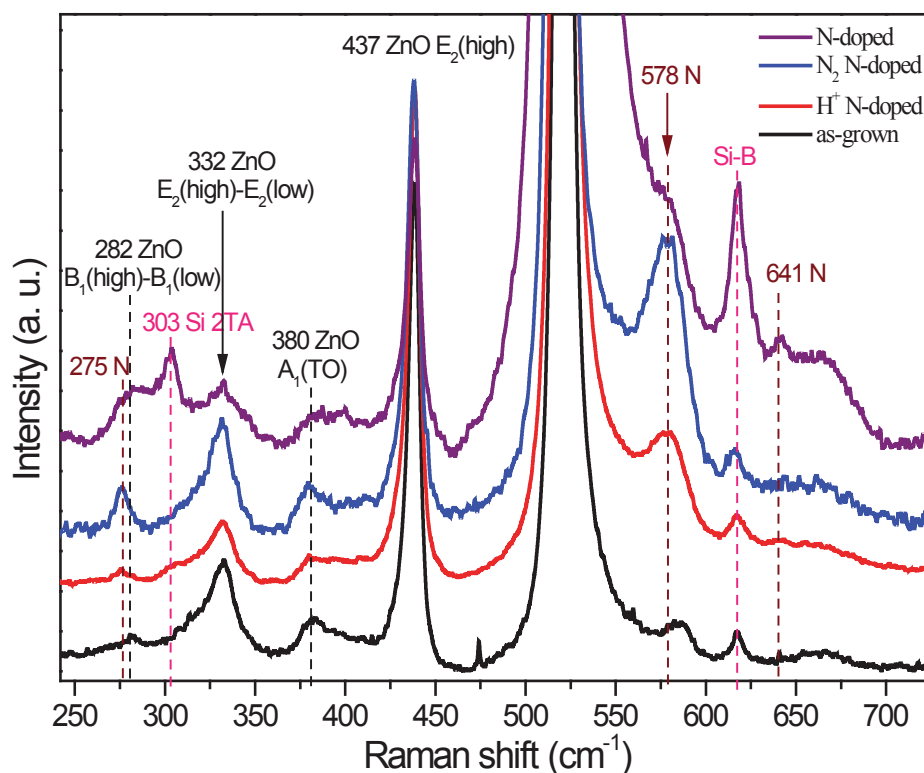


Figure 5.22. Raman spectra of ZnO nanowires processed using various treatments after growth, including rf N_2 plasma treatment, N_2 gas annealing, and rf H_2 plasma treatment. This set of nanowire samples were grown on Si substrates, so the dominant Raman peak around 525 cm^{-1} is excited from Si and are not fully displayed in the spectra.

As displayed in Figure 5.22, the Raman mode at 641 cm^{-1} disappears in the Raman spectrum of N-doped ZnO nanowires after annealing in N_2 gas, while the lattice exhibits stronger vibration at the Raman shift of 578 cm^{-1} , suggesting that the mode at 578 cm^{-1} is caused by the molecular nitrogen and the Raman scattering at 641 cm^{-1} should be ascribed to the atomic nitrogen species in ZnO. A weak Raman peak at 641 cm^{-1} appears again after the hydrogen plasma treatment on the N_2 gas annealed sample following N plasma doping, indicating that the Raman scattering at 641 cm^{-1} is caused by the formation of N-H bonds in ZnO. The post rf N plasma treatment incorporates a

huge amount of atomic nitrogen into ZnO nanowires, so the N-H bonds are easily formed between nitrogen ions and widespread hydrogen species at an adequate temperature. The annealing in N₂ gas after the N plasma helps to stabilise the nitrogen species in the lattice, while this heating treatment also breaks the N-H bonds and removes residual H atoms from ZnO.

The hydrogen plasma on the N₂ annealed ZnO nanowire sample introduces ionised hydrogen, which forms new N-H bonds with the atomic N, so the 641 cm⁻¹ peak reappears after the hydrogen plasma. It is noteworthy that N-related Raman scattering at 578 cm⁻¹ can be enhanced by either increasing the N plasma time or the annealing in N₂ gas after N plasma processing. Increasing the N plasma time converts more atomic nitrogen into loosely bound molecular N-N species, while annealing in N₂ gas after N plasma also increases the N₂ ratio in the nanowires, indicating that the anomalous Raman scattering at 578 cm⁻¹ in N-doped ZnO is directly induced by the molecular nitrogen scattered in the lattice.

The formation of N-H complexes has been a major concern when investigating the compensation effects of hydrogen donors on *p*-type conductivity of N-doped ZnO [168]. Hydrogen can form N-H bonds with atomic nitrogen in ZnO thus providing a route to increase the nitrogen concentration; while the hydrogen donor itself also compensates the nitrogen *p*-type carriers in the material. The assignment of 641 cm⁻¹ Raman vibrational mode to N-H bonds indicates that the atomic nitrogen can hardly lead to *p*-type conducted ZnO semiconductors because the commonly formed N-H complexes can neutralise the atomic nitrogen acceptors.

It is also significant to note that for all of the ZnO nanowire samples prepared via the

VPT growth using the one-zone tube furnace, no carbon-related Raman peaks, such as the D band at 1340 cm^{-1} and the G band at 1588 cm^{-1} [169], were shown in the spectra, indicating that the zinc and graphite admixture provides a stable Zn vapour source without the introduction of possible contamination.

5.4 Summary

To conclude, nitrogen-doped ZnO nanowires were achieved both by *in-situ* N_2O gas introduction and by post-growth rf nitrogen plasma annealing. Nitrogen doping in ZnO can eventually reach a threshold when using an unionised nitrogen source — N_2O — as the *in-situ* dopant gas. By utilising an ionised nitrogen source — rf nitrogen plasma — during the post growth treatment process, nitrogen species are incorporated throughout ZnO nanowires. The nitrogen K-edge XANES P_2 peak at 400.7 eV indicates the N $1s$ to π^* transition in the N-N species, is enhanced with the increase of the plasma treatment time. With increasing the rf nitrogen plasma time, a gradual blue shift of the Raman peak from $\sim 538\text{ cm}^{-1}$ to $\sim 551\text{ cm}^{-1}$ is observed, which is attributable to a relatively stable A_1 LA phonon overtone and the enhanced $2\text{B}_1(\text{low})$ mode. Persistent rf nitrogen plasma annealing causes the pair-up of atomic nitrogen species generating molecular nitrogen, which is confirmed to be an acceptor by establishing a correlation between the donor-acceptor pair peak intensity and the amount of molecular nitrogen species present in the sample. Molecular nitrogen acceptors in ZnO nanowires are found to be loosely bound to the host lattice rather than in atomic state.

Chapter 6 Hydrogen dopants in ZnO

6.1 Introduction to H-doping in ZnO

Interstitial hydrogen in ZnO can reside at the bond-centred (BC) site, H_{BC} , or the anti-bonding (AB) site (see Figure 6.1), H_{AB} , as theoretically predicted by Van de Walle [170]. Recently, Lavrov *et al.* demonstrated that the H_{BC} and H_O (hydrogen at oxygen vacancy site) are shallow donors in ZnO, and the PL emission at 3.36 eV is ascribed to H_{BC} [171], whereas other experimental evidence suggests that this peak is due to interstitial hydrogen in the $AB_{O,\perp}$ perpendicular alignment [172]. With no consensus achieved so far, the configuration and luminescence signatures of hydrogen in ZnO are still controversial due to the difficulty to directly probe the hydrogen states in the ZnO lattice.

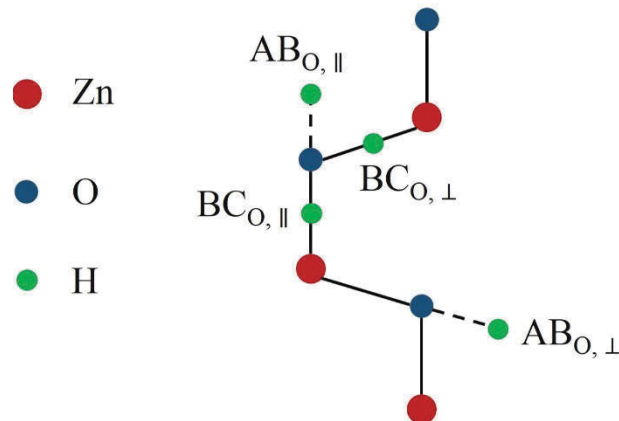


Figure 6.1. Schematic of the hydrogen configurations in ZnO wurtzite lattice structure (redrawn from Fig. 1 in [173]). The red, yellow and green circles represent Zn, O and H atoms, respectively.

Besides the I lines (see Table 2.2 in Chapter 2 for the characteristics of the I lines), a broad emission at an energy around 3.315 eV was commonly observed in the luminescence spectra of ZnO materials. This peak has been ascribed to a deep acceptor bound exciton (A^0X) [174] or free-to-bound recombination involving conduction band electron to acceptor-like defect transitions (e, A^0) [27]. Electron beam irradiation can be used to dissociate hydrogen from complexes [175], providing an effective method to investigate the correlation between the hydrogen bound excitons and the A line emission. Studies on the interfaces between wurtzite (WZ) and zinc blende (ZB) in ZnO have linked a broad emission at around 3.329 eV to the presence of basal plane stacking faults (BSFs) in the form of ZB quantum well in WZ matrix (WZ/ZB/WZ) [176]. Weston *et al.* [177] have observed the migration of H^+ in ZnO single crystals driven to the edge of the electron interaction volume under continuous electron beam irradiation. Recently, by using the surface-sensitive charge-based deep level transient spectroscopy (Q-DLTS), Ton-That *et al.* [36] found a surface defect state acting as shallow carrier trap with an activation energy of 11 ± 2 meV in H-doped ZnO. These results indicate the significant role of hydrogen in ZnO near-band-edge transitions.

By carrying out Fourier transform infrared (FTIR) spectroscopy measurements on H-doped ZnO single crystals, Jokela *et al.* [172] found that hydrogen aligns along tetrahedral Zn-O bonds with the O-H bond 110.6° diverging from the c -axis, which supports the identification that the anti-bonding hydrogen is in the $AB_{O,\perp}$ configuration, based on the XANES analysis. Incorporated hydrogen atoms have lower formation energy at $AB_{O,\perp}$ sites than at $AB_{O,\parallel}$ sites, yet they have almost the same bond length, so the interstitial hydrogen may preferentially align perpendicular to the c -axis, as predicted by Limpijumnong *et al.* [178] using the first-principles calculations. X-ray

absorption near-edge structure (XANES) spectroscopy using synchrotron X-ray, is a powerful tool for investigating the chemical bonding structure in materials, and provides a novel route for determining the hydrogen configuration in ZnO [179]. In this chapter, correlative techniques were used to investigate the site occupancy and optical signature of hydrogen in bulk ZnO.

6.2 Doping and characterisation of hydrogen in ZnO

A-plane ZnO single crystals, grown via a hydrothermal method by the MTI, USA, are used in this research. One *a*-plane single crystal sample was doped with hydrogen via plasma annealing at 200°C, as described in the “Experimental Methods” section (Section 3.2). XANES spectroscopy in the Total Electron Yield (TEY) mode was performed around the O *K*-edge and Zn *L*₃-edge on the Soft X-ray Spectroscopy beamline, Australian Synchrotron. The incident X-ray beam was linearly polarised and incident on the samples at different electric field to *c*-axis angles. The photon energy was calibrated using the Au 4 $f_{7/2}$ peak at 84 eV from a clean gold foil. An exhaustive review of the open literature suggests that this thesis reports the first investigation of the hydrogen configuration in ZnO using XANES spectroscopy. The CL signal was collected by a parabolic mirror attached to FEI Quanta 200 SEM and dispersed on the Hamamatsu CCD spectrometer through the Oriel MS257 monochromator.

6.3 Luminescence properties of H-doped ZnO

6.3.1 Temperature-resolved CL characterisation

Figure 6.2 displays the CL spectra of the as-grown and H-doped *a*-plane single crystals at incremental temperatures from 18 K to 200 K. The CL spectra of as-grown ZnO single crystal exhibit distinct fine spectral features at temperatures below 90 K:

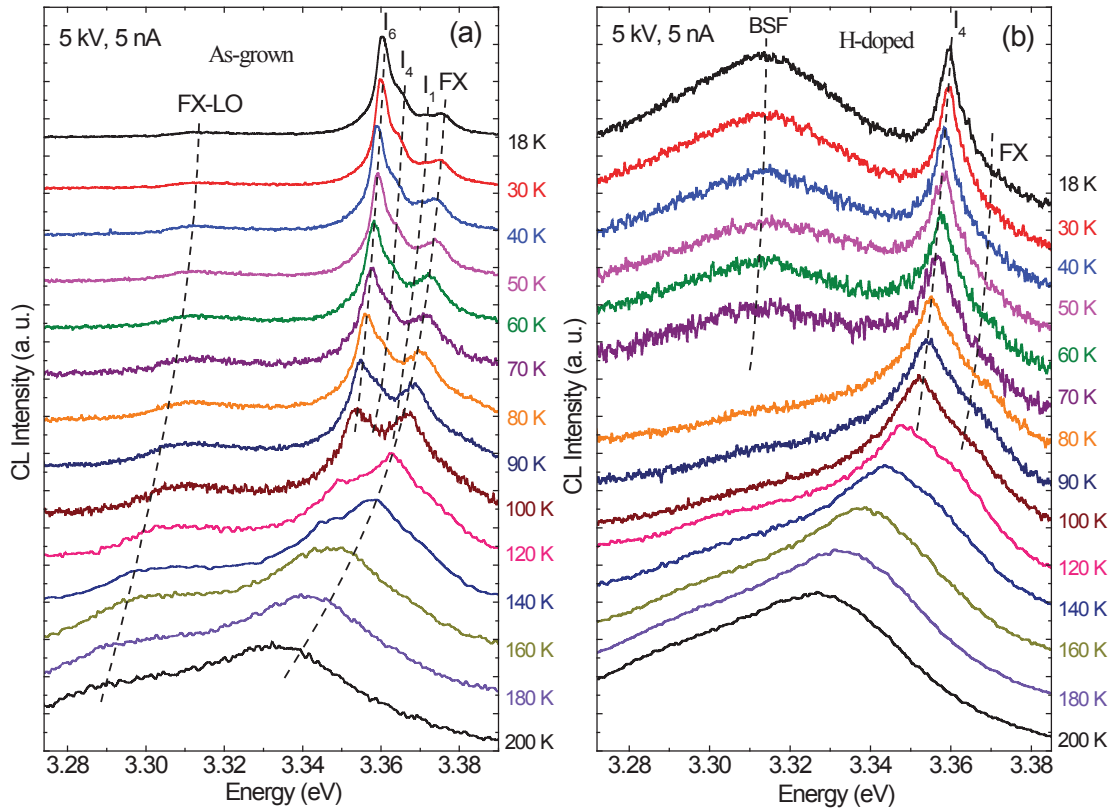


Figure 6.2. Temperature-resolved *a*-plane ZnO CL spectra of (a) as-received and (b) H-doped samples. The spectra of the H-doped ZnO exhibit broad *A* line emissions at 3.315 eV up to 70 K and suppressed free exciton shoulder. The *A* line in the H-doped sample disappears at temperatures above 80 K due to the thermal activation of extended defects.

free exciton (FX) at 3.375 eV, I_6 line at 3.360 eV and longitudinal phonon replicas separated by LO phonon energy $E_{LO} = 72$ meV, as shown in Figure 6.2(a) [180]. The FX emission is enhanced with increasing temperature due to the thermal detachment of bound excitons from shallow donors [58], and the I_6 line merges into the FX emission at temperatures above 160 K.

A sharp peak at 3.360 eV is observed in the spectra of the H-doped ZnO single crystal, as displayed in Figure 6.2(b), which is related to the incorporation of hydrogen shallow

donors and this peak can be labelled as the I_4 line due to its dominance in the CL spectra after hydrogen doping [56]. The I_6 line, which is the dominant emission in the NBE CL spectra of the as-received ZnO single crystal, becomes indistinguishable in the CL spectra of H-doped sample due to peak overlap with the I_4 line. After hydrogen plasma treatment, the FX emission is significantly suppressed at temperatures below 50 K due to the strong photon self-absorption. The FX peak emerges at 60 K and eventually overlaps with other I lines to form a single peak when the temperature reaches 160 K.

A strong, broad peak at 3.315 eV labelled as BSF emerges in the H-doped ZnO single crystal at temperatures from 18 K to 70 K. The broad BSF emission decreases in intensity with increasing temperature and finally disappears above 80 K, indicating that the hydrogen trapped in the BSFs becomes more susceptible to the electron beam irradiation with the temperature increase and is more likely to dissociate from the BSFs at higher temperatures. With the 5 nA electron beam at 5 kV used as the excitation source, nearly all the dissociated hydrogen migrates out from the defect sites within the electron-sample interaction volume at temperatures above 80 K.

6.3.2 Arrhenius plots of CL emissions from H-doped ZnO

Peak fitting enabled the intensities of the CL emission peaks at rising temperatures to be measured as a function of temperature. Corresponding Arrhenius plots in the logarithmic scale are displayed in Figure 6.3(a), (b) and (c), where the vertical axis is determined by calculating $\ln[I(0)/I(T) - 1]$, while the horizontal axis denotes the inverse temperature. Based on a previously established model, the luminescence intensity at temperature T can be expressed as [181]:

$$I(T) = I(0)/[1 + A\exp(-E_a/kT)], \quad (6.1)$$

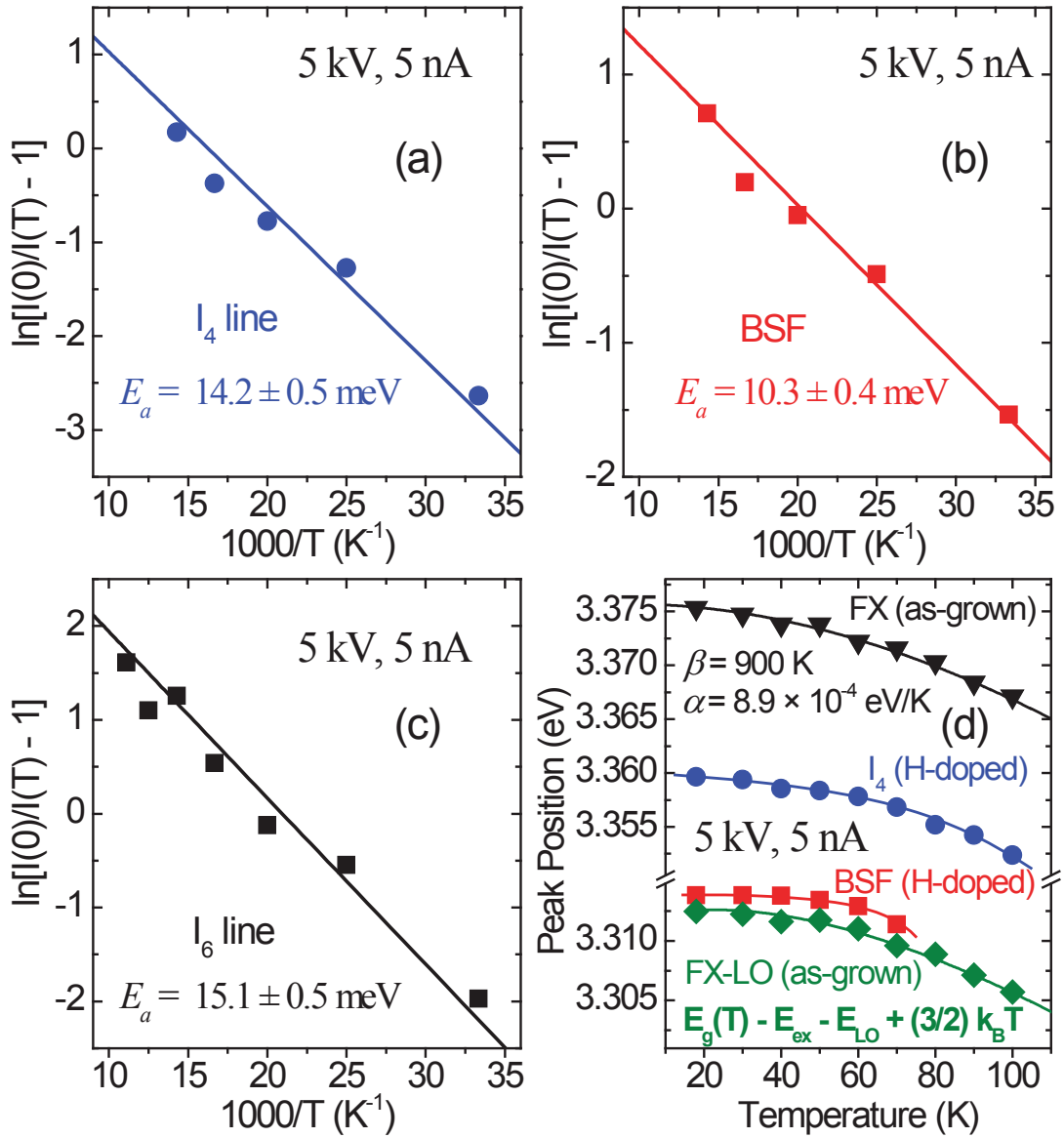


Figure 6.3. Arrhenius plots and peak energies of ZnO extracted from temperature-resolved CL spectra. (a), (b) and (c) show the Arrhenius plots of I_4 line, BSF emission of H-doped ZnO and I_6 line of the as-grown sample, respectively. The corresponding activation energy E_a is indicated in each figure. (d): temperature dependences of FX and FX-LO from the as-grown ZnO single crystal as well as the I_4 line and BSF emission from the H-doped sample. The peak positions are indicated using scatter symbols with black triangles, blue circles, red squares, and green diamonds representing the FX, I_4 line, BSF emission, and FX-LO. The red curve simulates the variation of the FX-LO peak position dependent on the temperature. The high voltage and e-beam current are 5 kV and 5 nA.

where $I(0)$ is the luminescence intensity at 0 K, E_a is the activation energy of the emission, and A is the scaling factor. The CL intensity Arrhenius plots of the I_4 line and the BSF emission peaks exhibit similar trends, and the temperature-dependent $\ln[I(0)/I(T) - 1]$ decreases linearly with the inverse temperature. By linearly fitting the data points using Equation (6.1), the activation energy E_a is derived as 10.3 ± 0.4 meV for BSF emission, 14.2 ± 0.5 meV for I_4 line, and 15.1 ± 0.5 meV for I_6 line. Low activation energy of BSF emission indicates that hydrogen in BSFs is more liable to external excitations.

The broad BSF emission emerges at similar energy position to FX-LO (3.312 eV) by coincidence. To elucidate the mechanisms behind these two emissions, we extracted the peak energies of FX and FX-LO for the as-grown ZnO single crystal from 18 K to 100 K as well as I_4 line and BSF emission for the H-doped sample. The peak energy of the ~ 3.315 eV emission decreases gradually at temperatures from 18 K to 70 K, but it follows a trend different from the FX from the as-grown ZnO and I_4 line for the H-doped sample. Such difference indicates that the broad peak at ~ 3.315 eV from the H-doped ZnO is not of exciton origin and should be closely related to hydrogen trapped in quantum well-like BSFs [30].

6.4 Site occupancy of hydrogen dopants

Figure 6.4(a) displays the O K -edge XANES spectra of the as-grown and H-doped ZnO single crystals, which reflect the transitions from O $1s$ states to unoccupied O $2p$ states. The spectra were collected with the incident X-ray normal to the sample surface and the electric vector $\vec{E}$ aligned at an angle of θ to the c -axis of the crystal, as shown in the inset of Figure 6.4(a). θ was set to be 0° , 45° and 90° for both the as-grown and the

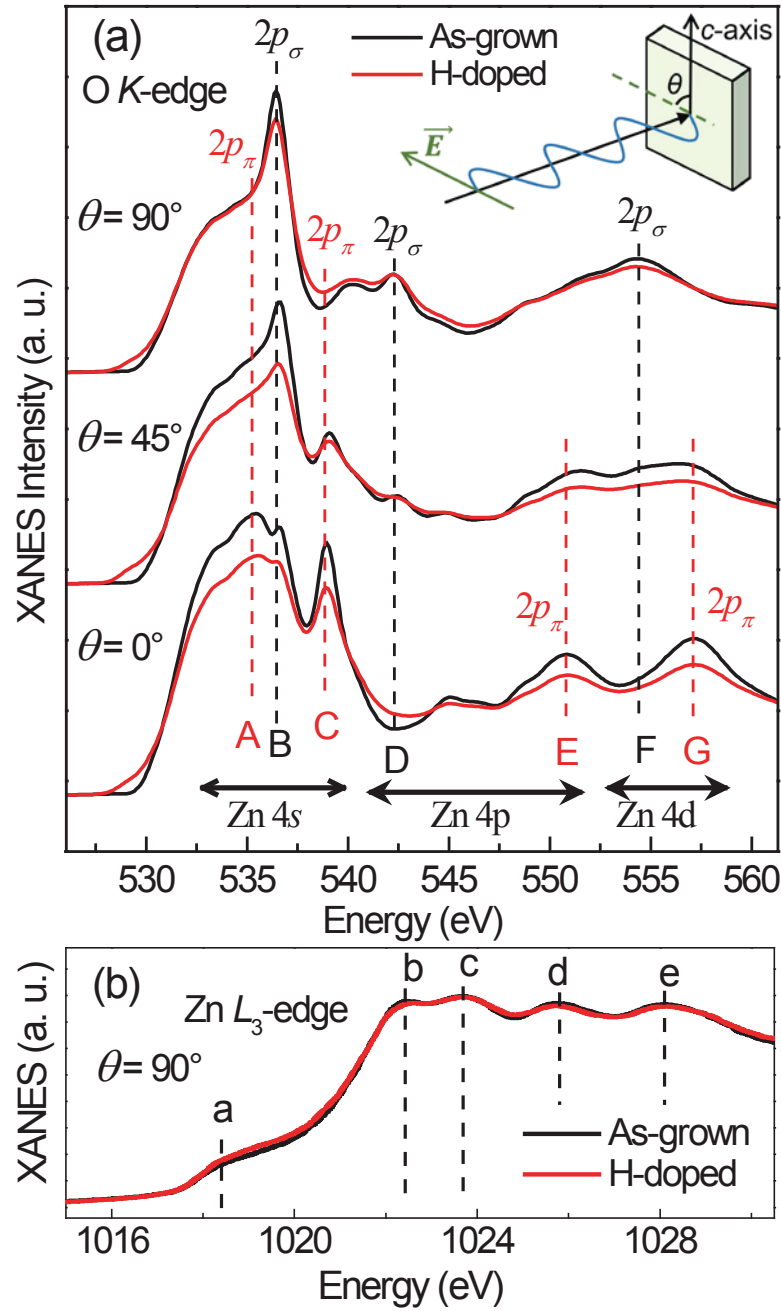


Figure 6.4. Angle-resolved O K-edge XANES spectra of as-received and H-doped ZnO single crystals collected in the TEY mode with the angle $\theta = 0^\circ$, 45° and 90° , as displayed in (a). The schematic shows the experimental configuration of the synchrotron X-ray irradiation on the a -plane ZnO sample with electric vector $\vec{E}$ and the c -axis of ZnO crystal at an angle θ . (b) shows the Zn L_3 -edge XANES spectra of as-received and H-doped a -plane ZnO single crystals with $\theta = 90^\circ$. No significant change is observed in the Zn electronic states after hydrogen doping.

H-doped ZnO samples. Features A–C are assigned to the O $2p$ states hybridised with Zn $4s$ states; absorption features D and E result from a mixture of the O $2p$ and Zn $4p$ states; while the peaks F and G are attributed to the hybridisation of Zn $4d$ with O $2p$ states [182]. When $\theta = 90^\circ$, the electron transitions from O $1s$ to O $2p_\sigma$ like orbitals — B, D and F — are at their strongest intensities because these transitions are perpendicular to the c -axis; when $\theta = 0^\circ$, the electron transitions from O $1s$ to O $2p_z$ like orbitals— A, C, E and G — are significantly enhanced because these transitions resonate parallel to the c -axis [183].

The polarised XANES is extremely sensitive to the geometric arrangement of the O bonds. Electronic transitions giving rise to XANES features can be approximated by a transition matrix element coupling the initial state $|i\rangle$ to the final state $\langle f|$ [184]:

$$\mu(\epsilon) = | \langle f | \mathbf{E} \cdot \mathbf{r} | i \rangle |^2 = A \cos^2\theta, \quad (6.2)$$

where $\mathbf{E}$ is the electric field vector, $\mathbf{r}$ the position vector of the absorbing atom, and θ the angle between the vectors $\mathbf{E}$ and $\mathbf{r}$. When the vector $\mathbf{E}$ is perpendicular to the c -axis ($\theta = 90^\circ$), B, D and F are at their strongest intensities as $2p_\sigma$ states have the largest projection on the electric field direction. When the vector $\mathbf{E}$ is rotated by 90° ($\theta = 0^\circ$), these peaks are at their lowest intensities while the absorption peaks A, C, E and G associated with the O $2p_\pi$ states are at their maximum intensities. This decomposition of the polarised XANES spectra into orbital-resolved states are entirely consistent with the calculated partial density of unoccupied states [183]. X-ray absorption features of electron transitions from O $1s$ state to both O $2p_\sigma$ and O $2p_\pi$ states are reflected in the XANES spectra collected at $\theta = 45^\circ$.

In contrast to the $2p_\sigma$ states which remain largely unchanged after the H doping, the $2p_\pi$ states are remarkably reduced, indicating the excess electron density along the c -axis orientation of the crystal. These results indicate that H binds predominantly parallel to the c -axis orientation, supporting the H_{BC} model in which strong O-H bonds are formed along the c -axis [185]. Figure 6.4(b) shows the Zn L_3 -edge XANES spectra of the as-grown and H-doped ZnO single crystals. Feature a has been ascribed to the Zn $2p$ to Zn $4s$ transition, while peaks b, c, d, and e result from the transition from Zn $2p$ to Zn $4d$ states [179]. No significant change is detectable in the Zn L_3 -edge XANES spectrum after H-doping (at both $\theta = 0^\circ$ and 90°), indicating that the electron transitions via Zn-H is nearly negligible because the chemical bond between two positively charged Zn and H atoms is very weak.

6.5 Hydrogen migration under electron beam irradiation

Time-resolved CL spectra from both the as-grown and H-doped ZnO single crystals are collected as a function of electron beam irradiation time to gain a greater understanding of the hydrogen dissociation kinetics of the BSF emission. In these measurements, the electron beam power was kept constant and the spectra were collected every 3 s with 1 s acquisition time for each spectrum. By increasing the electron beam current to 10 nA, a huge amount of energy is delivered onto the sample surface. Figure 6.5 displays the CL spectra of H-doped ZnO single crystals from 1 s to 22 s with a 3 seconds' increment between consecutive spectra. The left inset of Figure 6.5 shows the CL spectra of the as-grown ZnO at 1 s and 22 s, while the right inset displays the fitted intensities of the I_4 line and BSF emission as a function of the electron beam irradiation time. The FX and I lines in the CL spectra of the as-grown ZnO single crystal are virtually unaffected throughout the electron beam irradiation process, which

indicates that hydrogen and other impurity shallow donors are stable and are resistant to the e-beam irradiation [125].

In the time-resolved CL spectra of H-doped ZnO, the prominent surface 3.315 eV band decreases exponentially with irradiation time (right inset of Figure 6.5) and blueshifts upon the irradiation, while the I_4 line peak increases in intensity simultaneously and then decreases with its peak position unchanged. We attribute the dramatic decrease in this surface band to electron beam-induced disassociation of bound H dopants and electromigration of H_i^+ . First-principles calculations have previously shown that the binding energy of H bound at the BC site is 0.7 eV [185], which is well above the activation energy of BSF emission; therefore, the hydrogen species released from the surface BSFs are recaptured by the O-Zn bonds as H_{BC} causing the instantaneous intensity increase of the I_4 line.

Disassociation of H_{BC} may not necessarily lead to the loss of hydrogen since it can be recaptured in the absence of a local electric field, which explains why no H^+ migration occurs when the H-doped ZnO was irradiated by synchrotron X-rays. The time-dependent variation of the intensity of the 3.315 eV emission with electron irradiation is consistent with the theoretical prediction by Cazaux for the building-up of a surface charge layer under a high electron injection regime [186]. In this model, the electron beam induces a local electric field due to a positive surface region at the beam impact point after the emission of secondary electrons and a negatively charged layer in the bulk arising from trapped electrons [186].

A strong and broad peak at 3.315 eV is observed in the CL spectra after H-doping. A 5 keV electron beam probes the near-surface region of the ZnO single crystal and

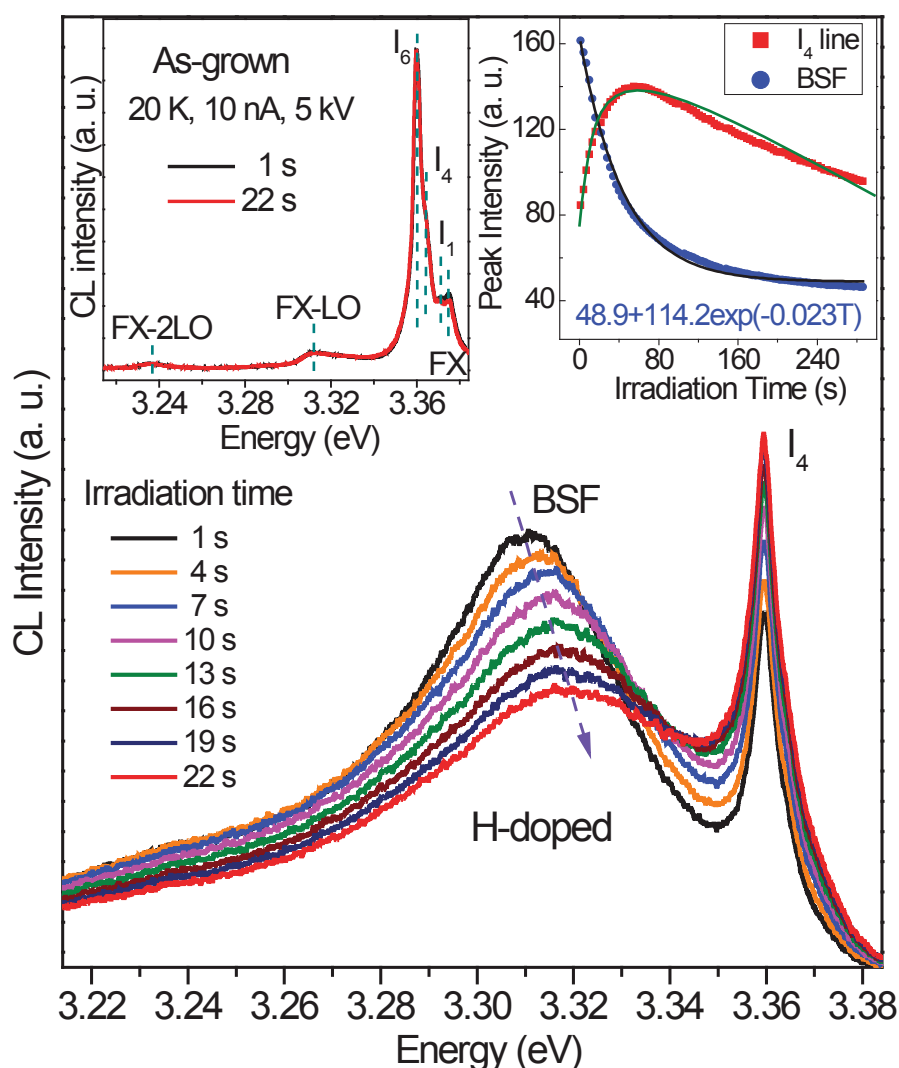


Figure 6.5. Time-resolved CL spectra of as-received and H-doped ZnO single crystals under high e-beam irradiation current (10 nA). The CL spectra were collected *in-situ* at a 3 s interval and an acquisition time of 1 s for each spectrum. The temperature is 20 K and the electron beam high voltage is 5 kV. The spectra in each figure are shifted vertically for clarity. The left inset shows the CL spectra of as-grown ZnO at 1 s and 22 s, and the right inset displays the fitted intensities of the I_4 line and BSF emission.

consequently the majority of the CL signal is generated from the surface layer of ~ 100 nm in thickness (see CASINO simulation results in Section 3.3.2.3). The intensity of the broad emission at 3.315 eV rapidly decreases with prolonged electron beam

irradiation, while the I_4 line exhibits fast increase at first and then slowly decreases under the irradiation. As shown in Figure 6.5, the intensity of the CL peak at 3.315 eV, which is stronger than the I_4 line at 1 s, becomes weaker with the electron beam irradiation time and reduces to only $\sim 1/2$ the original intensity at 22 s. Conversely the hydrogen trapped in BSFs can dissociate and migrate under the influence of sub-surface electric fields created by trapped charges. This proposed mechanism is supported by the findings that the activation energy of I_4 line in H-doped sample is higher than BSF emission, as shown in Figure 6.3(a) and (b). The concurrent blueshift of the BSF emission under e-beam irradiation could be attributed to the shrinkage of the potential well of the ZB regime in the ZnO WZ/ZB/WZ heterostructures [187].

During the irradiation, the incoming primary beam electrons that have given up all of their energy to the sample as well as thermalised secondary electrons can be trapped at defects. The positively charged layer is created in the near surface region of the crystal due to the emission of secondary electrons, leading to the build-up of an electric field. This field drives the mobile H^+ donors to the periphery of the electron-sample interaction volume, as shown in Figure 6.6(a).

The electron beam irradiation is conducted in spot mode, which covers much larger scale compared to the electron-sample interaction depth [~ 100 nm (see Figure 3.14)], so the negatively charged electron trapping layer produces a surface dipole, which is displayed in Figure 6.6(b). The simultaneous I_4 line increase and decrease can be explained by establishing a H^+ migration model: electrons trapped at the bottom of the interaction volume create a negative charge layer, while at the upper surface a positive charge layer is created with the secondary electrons escaping from the surface, as

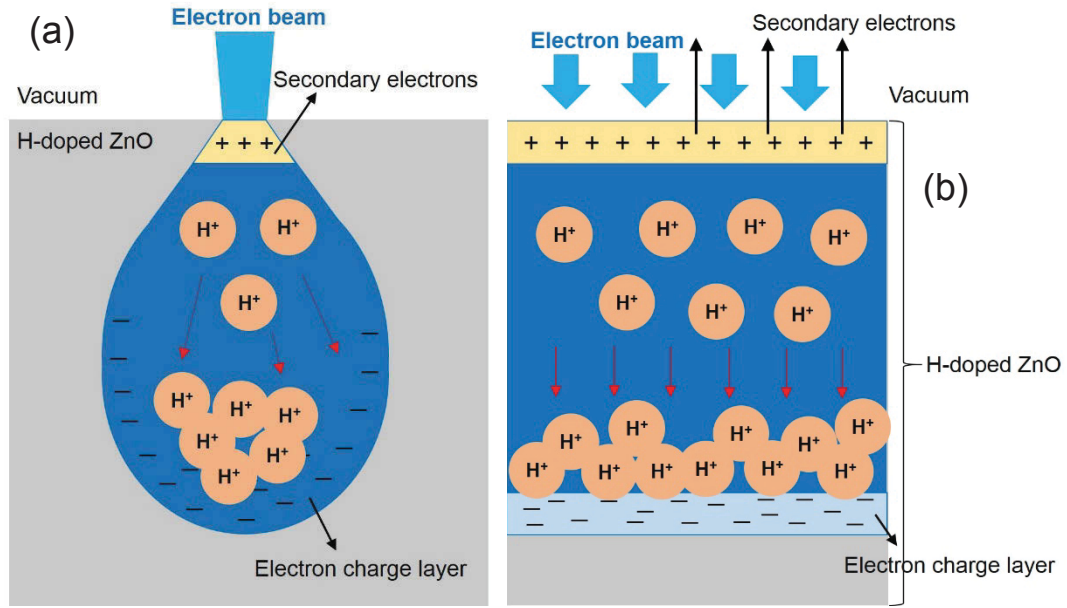


Figure 6.6. Schematic of the H donor migration under e-beam irradiation. The incident electrons create a positively charged layer in the near surface region and a negative charge layer ~ 100 nm under the surface, which drive the H donors to the periphery of the electron interaction volume. (a) shows the H⁺ movement under a stationary electron beam. (b) shows the charge distributions after the beam is scanned over a large area.

illustrated in Figure 6.6(b). These two oppositely charged layers create a surface dipole, which drives the free H⁺, dissociated by the e-beam from BSFs, towards the bottom of the interaction volume. In the early stages of diffusion, the H⁺ concentration increases near the maximum energy loss depth at 5kV thus increasing the I₄ intensity. Afterwards, the I₄ line intensity starts to decrease as the H⁺ diffuses past the maximum energy loss regime towards the bottom of the electron-sample interaction volume.

6.6 Summary

The optical properties of H-doping in ZnO single crystal has been investigated by means of CL and XANES spectroscopy measurements. Hydrogen shallow donors are

incorporated at the bond-centred sites by the formation of O-H bonds after the rf hydrogen plasma. A new broad peak was observed in the CL spectra of H-doped ZnO, which is ascribed to the emission induced by hydrogen trapped in the surface BSFs. The BSF emission decreases in intensity with hydrogen dissociating from the surface quantum well-like stacking faults under electron beam irradiation with high dose. The hydrogen donors are found to be in the BCO_{H} configuration when ZnO crystals are doped by plasma annealing.

Chapter 7 Conclusions and Outlook

7.1 Conclusions

It was found that the morphology of ZnO nanowires are highly sensitive to the thickness of Au catalyst film, the flow and pressure of oxygen during growth, and the morphology of Au nanodroplets that form as a result of annealing. The formed Au droplets have a significantly large distribution of sizes, which hinders the growth of nanowires with uniform diameters. ZnO nanowires have been successfully grown via the VS process by using either Au thin films or dropcast Au nanoparticles as catalyst. In addition, the catalytic role of Au nanoparticles in the ZnO vapour deposition was systematically investigated. The diameter of the ZnO nanowires was found to be larger as the density of Au nanoparticles increases. Remnants of green luminescence from the *a*-plane sidewalls of constituent nanowires were found within the coalesced nanowire. A nanowire bending model is established by investigating the Coulomb forces between the *c*-facets of nanowires. Optical characterisation shows that larger nanowires contain more oxygen vacancies than smaller ones. ZnO nanowires of different diameters can be grown using colloidal Au nanoparticles by simply controlling the Au nanoparticle concentration, which can provide a new route for obtaining diameter-controllable 1D ZnO nanostructures.

ZnO nanowires were successfully doped with nitrogen using a novel nitrogen plasma annealing method. Acceptor bound exciton (A^0X) was observed in the CL spectra of

N-doped ZnO nanowires and the donor-acceptor-pair recombination shows enhanced intensity with the enhancement of N-doping. By investigating the chemical states of the shallow acceptor in N-doped ZnO, a direct correlation between the intensity of a DAP centred at 3.232 eV and the concentration of N_2 molecular species that weakly bond to the ZnO lattice was established. These results indicate that the DAP in ZnO is due to the recombination involving shallow acceptors induced by $(N_2)_{Zn}$ and shallow donors. The formation of N_2 molecule is found to be controlled by the oxygen vacancy assisted diffusion mechanism. The existence of N_2 as a shallow acceptor state has important implications on the growth strategies for *p*-type ZnO.

Optical properties induced by H-doping in ZnO single crystal were investigated by means of CL and XANES spectroscopy. The XANES results reveal that hydrogen is incorporated at the bond-centred sites via the formation of O-H bonds after hydrogen plasma annealing. High resolution CL analysis reveals the evolution of I_4 line under electron beam irradiation, which is attributable to interstitial hydrogen shallow donors. A new broad peak at 3.315 eV was observed in the CL spectra of H-doped ZnO, which is assigned as the BSF emission caused by the hydrogen trapped in the surface basal plane stacking faults.

7.2 Suggestions for future work

Vertically aligned ZnO nanowires have been successfully grown on silicon and sapphire substrates using Au catalyst. Parallel to the attempts of fabricating *p*-type conducted ZnO nanowires by nitrogen doping, enhancing the *n*-type conductivity of this material has also been the focus of the scientific community. Compared to the volatile hydrogen dopants, transition metal elements, e.g., Al, In and Ga, are shallow

donors and are more stable in ZnO nanowires. As reported previously, Al-doped ZnO showed strong UV emission compared to undoped ZnO due to the incorporation of Al donors. Ga is also regarded as one of the most effective *n*-type dopants because it possesses an atomic radius similar to Zn while has low electronegativity. Al doping in ZnO nanowires has been realised by adding Al powder into the ZnO and graphite mixture source material, while Ga-doped ZnO nanowires can be grown using Ga₂O₃ as the Ga source during the VPT ZnO nanowire growth. The introduction of the impurities, such as Ga or Al during nanowire growth, may allow a new route to tune the electronic properties of nanowires for nanoscale plasmonic applications.

The nitrogen doping of ZnO nanowires were investigated during the course of this work that could be the topic for further research. It would be highly interesting to investigate the nanowires co-doped with nitrogen and hydrogen. This co-doping could potentially passivate non-radiative defects in nanowires as well as stabilise nitrogen acceptors, similar to the formation of Mg-H complexes in GaN. It would also be interesting to carry out ESR measurements to identify nitrogen species and their complexes in ZnO nanowires.

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