

**Doped ZnO nanostructures for optoelectronics:
growth, properties and devices**

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

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January 2019

Declaration of Authorship

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as part of the collaborative doctoral degree and/or fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This research is supported by an Australian Government Research Training Program Scholarship.

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Abstract

Zinc oxide (ZnO) semiconductor is a highly attractive material for optoelectronic and photonic applications due to its high exciton binding energy (60 meV) and large bandgap (3.37 eV) at room temperature. In addition, ZnO doped with group III elements is a promising system for wavelength-tunable plasmonics because of its low absorption loss in the infrared region compared with metals. However, poor understanding of native defects and of their interaction with impurities has limited the development of practical ZnO-based photonic and plasmonic devices. The primary aim of this project was to investigate the effects of the incorporation of donor and acceptor impurities on the optoelectronic properties of ZnO nanostructures and to exploit new properties in optoelectronic devices.

First, Li dopants were used to produce multi-colour emitting ZnO films fabricated by the spray pyrolysis technique. The pyrolytic films exhibit multi-colour emissions of yellow, green and blue, which can be tuned by varying the Li concentration. Simulation of the cathodoluminescence spectra from the Li-doped films using the Huang-Rhys model enables the determination of the energy levels of luminescence centres and their electron-phonon coupling strength. These centres are attributable to either V_{Zn} or Li_{Zn} acceptor states.

Second, Ga was used to enhance the electrical and optical properties of ZnO nanorods. A large number of ZnO nanowires and nanorods were fabricated with various Ga concentration up to 1.4 at% by the vapour phase transport method. It was found that Ga incorporation activates the Cu luminescence centres, which lead to the emergence of a characteristic fine structure in the green luminescence (GL) band of ZnO. The emergence of the structured GL is due to the Cu^+ state being

stabilized by the rise in the Fermi level above the $0/-$ ($\text{Cu}^{2+}/\text{Cu}^+$) charge transfer level as a result of Ga donor incorporation. From a combination of optical characterisation and simulation using the Brownian oscillator model, the doublet fine structures are shown to originate from two hole transitions with the Cu^+ state located at 390 meV above the valence band.

Third, bandgap engineering in a single ZnO microrod was demonstrated through crystal defect mediation. ZnO microrods with graded distribution of Ga dopants were fabricated by the vapour phase transport method. The near-band-edge (NBE) emission of the graded microrods was found to be red shifted by ~ 0.6 eV due to the merging of Ga-related impurity bands with the ZnO energy bands, consistent with the bandgap shift as calculated by the Density Function Theory. The results demonstrate self-regulation of charged defect compensation and the possibility of multi-wavelength light sources within a microrod.

Finally, Ga-doped ZnO nanorods were optimised and electrically integrated into Si-based photonic devices in order to fabricate light emitting diodes (LEDs). LEDs fabricated from the Ga-doped ZnO nanorod/p-Si heterojunction display bright and colour-tunable electroluminescence (EL). These nanorod LEDs possess a dramatically enhanced performance and an order of magnitude higher EL compared with equivalent LED devices made with pristine nanorods. These results point to an effective route for large-scale fabrication of conductive, single-crystalline Ga-doped ZnO nanorods for photonic and optoelectronic applications.

Acknowledgements

First of all, I express my profound gratitude to my supervisors A/Prof. Cuong Ton-That, Prof. Matthew Ronald Phillips, Dr. Angus Gentle for their constructive criticism, continuous guidance, and inspiration in conducting my PhD research and writing up this thesis. I would like to thank Geoff McCredie, Katie McBean, Herbert Yuan, and Mark Berkahn for giving me the valuable technical support in my experimental work in the Microstructural Analysis Unit.

I appreciate the assistance of Sumin Choi and Saskia Fiedler have provided me in photoluminescence and X-ray photoelectron spectroscopy experiments, respectively. I am grateful to Sajid Ali, my friend, for helping with theoretical bandgap calculations of Ga-doped ZnO. I would like to thank Mika T. Westerhausen for the ICP-MS measurements of Ga-doped ZnO nanowires. I am also grateful to John Scott for his useful advice on TEM. I am also thankful to Liangchen Zhu and Olivier Lee for their valuable tips and suggestions on the use of the cathodoluminescence spectrometer.

Finally, I would like to express my special gratefulness to my family, especially Urfi Tabassum, for their moral support and sustaining inspiration. This dissertation would never be possible without their love and affection.

List of Publications

Journal papers

1. **M. Azizar Rahman**, Matthew R. Phillips, Cuong Ton-That, “Efficient multi-coloured Li-doped ZnO thin films fabricated by spray Pyrolysis” Journal of Alloys and Compounds, 691 (2017) 339.
2. **M. Azizar Rahman**, Mika T. Westerhausen, Christian Nenstiel, Sumin Choi, Axel Hoffmann, Angus Gentle, Matthew R. Phillips, and Cuong Ton-That, “Charge state switching of Cu acceptors in ZnO nanorods”, Applied Physics Letters, 110 (2017) 121907.
3. **M. Azizar Rahman**, John A. Scott, A. Gentle, Matthew R. Phillips, Cuong Ton-That, “A facile method for bright, colour-tunable light-emitting diodes based on Ga-doped ZnO nanorods, Nanotechnology, 29 (2018) 425707.
4. **M. Azizar Rahman**, Sajid Ali, Michael J. Ford, Matthew R. Phillips, and Cuong Ton-That, “Ga-mediated optical emission from ZnO microrods”, in preparation.
5. A. M. M. Tanveer Karim, **M. Azizar Rahman**, M. Sazzad Hossain¹, M. K. Rahman Khan, M. Mozibur Rahman, M. Kamruzzaman and Cuong Ton-That “Multi-Colour Excitonic Emissions in Chemical Dip-Coated Organolead Mixed-Halide Perovskite”, Chemistry select, 3 (2018) 1

Conference presentations

1. **M. Azizar Rahman**, Matthew R. Phillips, Cuong Ton-That, “Structured green emission band and electron-phonon coupling in Ga-doped ZnO nanowires”, ICONN, 7 – 11 February 2016, Canberra, Australia.
2. **M. Azizar Rahman**, A. Gentle, Matthew R. Phillips, Cuong Ton-That, “Activating the Cu acceptors in ZnO nanorods by Ga doping”, ICONN, 29 January – 2 February 2018, Wollongong, Australia.

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List of Acronyms

$A^{\circ}X$	Neutral acceptor bound exciton
AFM	Atomic force microscope
BL	Blue luminescence
CL	Cathodoluminescence
CVD	Chemical vapour deposition
CCD	Charge-coupled device
CTL	Charge transfer level
$D^{+}X$	Ionised donor bound exciton
$D^{\circ}X$	Neutral donor bound exciton
DAP	Donor acceptor pair
DL	Deep level
DFT	Density function theory
DOS	Density of state
EL	Electroluminescence
EDS	Energy dispersive spectroscopy
FWHM	Full width at half maximum
FX	Free exciton
GL	Green luminescence
GGA	Generalized gradient approximation
LED	Light Emitting diode
LDA	Local density approximation
LA-ICP-MS	Laser ablated inductively coupled plasma mass spectroscopy
LO	Longitudinal optics
MBO	Multimode Brownian oscillator
MOCVD	Metal-organic chemical vapour deposition
MBE	Molecular beam epitaxy
NBE	Near-band-edge emission
NIST	National institute of standard and technology

NIR	Near infrared region
NRs	Nanorods
PL	Photoluminescence
PMMA	Poly-methyl-methacrylate
PEDOT	Poly(3,4-ethylenedioxythiophene)
RL	Red luminescence
SEM	Scanning electron microscope
SEAD	Selected area diffraction
TEM	Transmission electron microscope
UV	Ultraviolet
VPT	Vapour phase transport
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
YL	Yellow luminescence
ZPL	Zero phonon line