UNIVERSITY OF TECHNOLOGY, SYDNEY

Luminescence Studies of ZnO Crystals and Nanowires

by

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Declaration of Authorship

I, Matthew Foley, declare that this thesis titled,

'Luminescence Studies of ZnO Crystals and Nanowires'

and the work presented in it are my own. I confirm that:

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- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
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"There is a theory which states that if ever anyone discovers exactly what the Universe is for and why it is here, it will instantly disappear and be replaced by something even more bizarre and inexplicable.
There is another theory which states that this has already happened."

- Douglas Adams

"There are two possible outcomes: if the result confirms the hypothesis, then you've made a measurement. If the result is contrary to the hypothesis, then you've made a discovery."

- Enrico Fermi

Abstract

ZnO is a direct semiconductor with a band gap of 3.4 eV at room temperature making it a hot topic for optoelectronic research across a broad range of applications. The current solid state lighting technology typically uses nitride semiconductors in the generation of light, more commonly gallium nitride. ZnO is a more efficient light generator than GaN owing to its high excitonic binding energy, and for this reason, ZnO is a potential material that may soon compete with GaN as a cornerstone of the solid state lighting revolution. Significant obstacles preventing the wide scale usage of ZnO include the lack of reliable p-type doping and high degree of uncertainty surrounding the nature of its defects, intrinsic n-type conductivity and optical properties.

The aim of this thesis is therefore to explore the luminescence and defect properties of doped and undoped ZnO nanowires and crystals.

During the project, ZnO nanowires were grown through a vapour deposition method under varying growth conditions. Changes in the choice of substrate, gas flows, pressures, and growth times were linked to changes in the structural and optical properties of the nanowires as characterised by scanning electron imaging and complementary spectroscopic techniques. Gold coated epitaxially matched sapphire substrates positioned close to the source material were found to produce highly aligned nanowires arrays. Cathodoluminescence (CL) imaging showed a localisation of defect luminescence near the surface of ZnO nanowire sidewalls. Oxygen deficiencies were also found to be localised on the sidewalls of the nanowires, supporting a correlation between green luminescence and oxygen vacancies in ZnO.

Post processing plasma modification of ZnO crystals and powders were used to identify defects contributing to the observable green luminescence. The defect emissions

were fitted with constrained Gaussian peaks which were linked to multiple competitive radiative centres. Variations in the near band edge (NBE) to green defect intensity ratios were also investigated to assist in the assignment of the defect peaks.

Incorporation of transition metals into ZnO was achieved through thermal in-diffusion and sol-gel preparation methods. Significant quenching of the defect related optical emissions relative to the UV emission was observed for both Mn doped samples, while an enhancement of the defect emission was observed near the surface of Fe doped crystals. Monochromatic CL imaging was shown to be an effective method of determining the depth of iron incorporation in iron doped ZnO crystals owing to the enhancement of the green emission.

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List of Publications and Presentations

Refereed Journal Publications

C. Ton-That, M. Foley, L.L.C. Lem, G. McCredie, M.R. Phillips, B.C.C. Cowie. Diffusion synthesis and electronic properties of Fe-doped ZnO.
Mat. Lett. 64, 3, 386-388, 2010.

M. Foley, C. Ton-That and M. R. Phillips. Luminescent properties of ZnO structures grown with a vapour transport method.
Thin Solid Films 518, 15, 4231-4233, 2010.

M. Foley, C. Ton-That and M. R. Phillips. Cathodoluminescence inhomogeneity in ZnO nanorods.
Appl. Phys. Lett. 93, 243104, 2008.

C. Ton-That, M. R. Phillips, M. Foley, S. J. Moody and A. P. J. Stampfl. Surface Electronic Properties of ZnO Nanoparticles.
Appl. Phys. Lett. 92, 26, 1-3, 2008.

C. Ton-That, M. Foley, and M. R. Phillips. Luminescent properties of ZnO nanowires and as-grown ensembles.
Nanotechnology 19, 415606, 2008.

Oral Presentations

M. Foley, C. Ton-That and M. R. Phillips. Spatially Inhomogeneous Defect Distribution in ZnO Nanorods.
Australian Microbeam Analysis Society XI, Canberra. February 2011.

M. Foley. Luminescence inhomogeneity in ZnO nanorods.
Australian Institute of Physics, NSW Branch, Postgraduate Awards. 2010.

M. Foley, C. Ton-That and M. R. Phillips. Cathodoluminescence characterisation of vapour transport grown ZnO structures.
2010 International Conference On Nanoscience and Nanotechnology, Sydney. February 2010.

M. Foley, C. Ton-That and M. R. Phillips. Local electronic structure and luminescence properties of ZnO nanowires.
SPIE Microeletronics, MEMS and Nanotechnology, Canberra. December 2007.

Poster Presentations

M. Foley, C. Ton-That and M. R. Phillips. Zinc oxide nanostructures and their cathodoluminescent properties.
NSW Branch of Materials Australia Jules Byrnes Student Presentation Evening. 2009.

C. Ton-That, M. Foley and M. R. Phillips. Luminescence properties of ZnO nanowires and as-grown ensembles.
SPIE Microeletronics, MEMS and Nanotechnology, Canberra. December 2007.

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Common Acronyms

Notation	Description
A^0X	acceptor bound exciton.
AFM	atomic force microscope.
ARPES	angle resolved photoemission spectroscopy.
CL	cathodoluminescence.
CVD	chemical vapour deposition.
D^0X	donor bound exciton.
DCL	depth-resolved cathodoluminescence.
DFT	density functional theory.
DL	deep level.
DLE	deep level emission.
DMS	dilute magnetic semiconductor.
FWHM	full width at half maximum.
GL	green luminescence.
LED	light emitting diode.
LO	longitudinal optical.

Notation	Description
NBE	near band-edge.
PDCL	power-density resolved cathodoluminescence.
PES	photoemission spectroscopy.
PL	photoluminescence.
sccm	standard cubic centimetres per minute.
SEM	scanning electron microscope.
SLS	synchrotron light source.
TM	transition metal.
UV	ultraviolet.
UV-Vis	ultraviolet-visible spectroscopy.
VLS	vapour-liquid-solid.
VS	vapour-solid.
VSS	vapour-solid-solid.
XANES	x-ray absorption near edge structure.
XPS	x-ray photoemission spectroscopy.
XRD	x-ray diffractometry.