UNIVERSITY OF TECHNOLOGY SYDNEY

Doping and Characterisation of ZnO Nanowires and Crystals

by

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Declaration of Authorship

I, Liangchen Zhu, hereby declare that the work in this thesis has neither previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text. I confirm that:

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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.

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List of Publications and Presentations

Journal papers

L. Zhu, C. Ton-That, and M. R. Phillips, Nitrogen incorporation in ZnO nanowires using N_2O dopant gas. Mater. Lett. **99**, 42-45 (2013).

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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 N_2O 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^0X	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^0X	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