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

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# 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.

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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/- ($Cu^{2+}/Cu^{+}$) 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.

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# 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 Hossain[1], 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 |