UNIVERISTY OF TECHNOLOGY SYDNEY

THE EFFECT OF SURFACE DEFECTS ON THE OPTICAL AND ELECTRICAL PROPERTIES OF ZnO NANORODS

by

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Declaration of Authorship

I, Suranan Anantachaisilp, declare that this thesis titled, “The Effect of Surface Defects on the Optical and Electrical Properties of ZnO Nanorods” and the work presented in it is my own. I confirm that: This work was done wholly or mainly while in candidature for a co-tutelle research degree at this University and the Mahidol University.

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ABSTRACT

This thesis reports on the effect of native point defects on both the NH_3 gas sensing properties and the surface electronic structure of ZnO nanorods. Low temperature hydrothermal growth at 90°C was utilised to synthesize ZnO nanorods approximately 55 ± 5 nm in diameter. The type and density of intrinsic surface defects on the ZnO nanorod was controlled using post growth annealing in O_2 gas and Zn vapor environments. Low voltage cathodoluminescence (CL) spectroscopy confirmed that the heat treatment process produced different surface defect structures. The as-grown, O_2, and Zn annealed nanorods exhibited broad CL peaks centered at 1.90 eV (YL), 1.70 eV (RL), and 2.44 eV (GL), which were attributed to O interstitials or Li_{Zn} deep acceptors, acceptor-like V_{Zn} complexes, and donor-like V_O related centers, respectively.

The first part of this thesis focuses on the influence of deep level surface defects on NH_3 gas response of ZnO nanorods. Electrical and gas sensing measurements revealed that the NH_3 gas sensitivity was 4.1 for the as-grown (YL), 22.6 for O_2 anneal (RL), and 1.4 for Zn vapor anneal (GL) samples. Hydrogen plasma treatment quenched the RL and inverted the ammonia electrical response due to the incorporation of shallow hydrogen donors. Changes to the gas sensing response were attributed to a shift in the ZnO Fermi level position relative to the ammonia gas chemical potential due to the formation near surface donor or acceptor centers.

In the second part of this thesis the effect of native point defects on the surface electronic structure of all ZnO nanorod samples was studies utilizing X-ray photoemission spectroscopy (XPS), X-ray Absorption Near-Edge Structure (XANES), electron spin resonance (ESR), low voltage CL spectroscopy, sub band gap photoluminescence (PL) spectroscopy and electrical I-V measurements. Correlative characterization measurements established that the degree of surface band bending and surface conductivity is controlled by the amount of adsorbed ambient gas species (O_2, H_2O and OH), which is mediated by type and concentration of intrinsic surface point defects.

The last part of this thesis concentrates on the chemical origin of RL peak and its optical properties. A wide range of analysis techniques, including PL and CL

spectroscopy, XANES and ESR was used to comprehensively characterize the RL emission. From these data, the RL has been assigned to highly lattice coupled V_{Zn}-related acceptor-like center. No correlation was found between the RL and nitrogen impurities.

KEY WORDS: ZnO NANORODS, HYDROTHERMAL GROWTH, SURFACE ELECTRONIC PROPERTIES, GAS SENSING PREOPERTIES, RED LUMINESCENCE

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Refereed Journal Publications

S. Anantachaisilp, S.M. Smith, C. Ton-That, S. Pornsuwan, A.R. Moon, C. Nenstiel, A. Hoffmann, M.R. Phillips, Nature of Red Luminescence in Oxygen Treated Hydrothermally Grown Zinc Oxide Nanorods, *Journal of Luminescence*, **168** (2015) 20-25.

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LIST OF ACRONYMS

A^0	Neutral acceptor
BB	Band bending
BX	Bound exciton
CB	Conduction band
CC	Configurational coordinate
CCD	Charge-coupled device
CL	Cathodoluminescence
D^0X	Neutral donor bound exciton
DAP	Donor-acceptor pair
DL	Deep level
EPR	Electron paramagnetic resonance
ESR	Electron spin resonance
FBT	Free-to-bound transition
FWHM	Full width at half maximum
FX	Free exciton
GL	Green luminescence
HMT	Hexamethylene tetramine
I-V	Current-Voltage

LIST OF ACRONYMS (cont.)

LO	Longitudinal optical
NBE	Near band edge
OL	Orange luminescence
PL	Photoluminescence
RL	Red luminescence
S	Sensitivity
sccm	standard cubic centimetres per minute
SEM	Scanning electron microscopy
TEY	Total electron yield
TFY	Total fluorescence yield
UV	Ultra-violet
VB	Valence band
XANES	X-ray absorption near edge spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-Ray diffraction
YL	Yellow luminescence