

UNIVERSITY OF TECHNOLOGY SYDNEY

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

by

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the degree of Doctor of Philosophy

in the

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Faculty of Science

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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 studied 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 PROPERTIES, RED
LUMINESCENCE

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CONTENTS

	Page
Declaration of Authorship	i
ABSTRACT	ii
ACKNOWLEDGEMENTS	iv
LIST OF PUBLICATIONS	x
LIST OF TABLES	xi
LIST OF FIGURES	xii
LIST OF SCHEMES	xx
LIST OF ACRONYMS	xxi
CHAPTER I INTRODUCTION TO ZINC OXIDE	1
1.1 Motivation of the Research	2
1.2 Objectives of the Research	4
1.3 Thesis Outline	5
CHAPTER II OPTICAL, ELECTRICAL, AND GAS SENSING	6
PROPERTIES OF ZnO AND ITS SYNTHESIS: LITERATURE REVIEWS	
2.1 Physical and Chemical Properties of ZnO	6
2.1.1 Crystal Structure	7
2.1.2 Electronic Band Structure	8
2.1.3 Defect Chemistry	9
2.1.3.1 Vacancies	12
2.1.3.2 Interstitials	14
2.1.3.3 Antisites	15
2.1.3.4 Impurities	15
2.1.3.5 Formation Energies and Processes of Native Defects	16
2.2 Optical Properties and Processes in ZnO	19
2.2.1 Excitons	20

CONTENTS (cont.)

	Page
2.2.2 Radiative Recombination	21
2.2.2.1 Near Band Edge Emission	21
2.2.2.2 Defect-Related Deep Level Emission	22
2.2.2.2.1 Green Luminescence	24
2.2.2.2.2 Yellow Luminescence	25
2.2.2.2.3 Red Luminescence	25
2.2.3 Temperature-Dependence Luminescence	26
2.3 Electrical Properties of ZnO	26
2.3.1 Ohmic Contacts to ZnO	27
2.3.2 Schottky Contacts to ZnO	28
2.4 Gas Sensing Properties of ZnO	28
2.4.1 Gas Sensor Characteristics	29
2.4.1.1 Sensitivity	29
2.4.1.2 Selectivity	29
2.4.1.3 Response Time and Recovery Time	30
2.4.2 Gas Sensing Mechanisms of ZnO	31
2.4.2.1 Oxidative Gas	32
2.4.2.2 Reductive Gas	33
2.4.2.2.1 Ammonia Gas	34
2.5 Synthesis of ZnO Nanostructures	34
2.5.1 High Temperature Approaches	35
2.5.2 Low Temperature Approaches	35
2.5.2.1 Hydrothermal Growth	35
CHAPTER III CHEMICALS AND EXPERIMENTAL DETAILS	38
3.1 Chemicals and Instruments	38
3.2 Sample Preparation	38

CONTENTS (cont.)

	Page
3.2.1 ZnO Nanostructures Growth	39
3.2.1.1 Seed Layer Deposition	39
3.2.1.2 Hydrothermal Growth	40
3.2.2 Post Growth Processing	40
3.2.2.1 Annealing	40
3.2.2.2 Hydrogen Plasma Treatment	41
3.3 Scanning Electron Microscopy (SEM)	42
3.4 X-Ray Diffraction (XRD)	43
3.5 Cathodoluminescence Spectroscopy (CL)	44
3.6 Photoluminescence Spectroscopy (PL)	46
3.7 Synchrotron Light Experiments	46
3.7.1 X-Ray Photoelectron Spectroscopy (XPS)	47
3.7.2 X-Ray Absorption Near Edge Spectroscopy (XANES)	47
3.8 Electrode Deposition and Gas Sensor Device Assembly	48
3.9 Current Voltage Characteristic Measurement	49
3.10 Gas Sensing Measurement	49
3.10.1 Gas Measurement System	50
3.10.2 Designed experimental procedures	51
CHAPTER IV TAILORING DEEP LEVEL SURFACE DEFECTS IN ZnO	53
NANORODS FOR HIGH SENSITIVITY AMMONIA GAS	
SENSING	
4.1 Summary	53
4.2 Introduction	53
4.3 Experimental Section	55
4.3.1 Synthesis of ZnO Nanorods and Post-Growth Processing	55

CONTENTS (cont.)

	Page
4.3.2 Analysis Techniques	55
4.3.3 Fabrication of ZnO Nanorods Gas Sensor and Gas Sensing Measurement	56
4.4 Results and Discussion	56
4.5 Conclusions	66
CHAPTER V THE SURFACE ELECTRONIC STRUCTURE OF ZnO NANORODS: THE ROLE OF SURFACE DEFECTS	68
5.1 Summary	68
5.2 Introduction	68
5.3 Experimental Section	69
5.4 Results and Discussion	71
5.5 Conclusions	83
CHAPTER VI NATURE OF RED LUMINESCENCE IN OXYGEN TREATED HYDROTHERMALLY GROWN ZINC OXIDE NANORODS	84
6.1 Summary	84
6.2 Introduction	84
6.3 Experimental Section	85
6.3.1 Preparation and Post Growth Processing of ZnO Nanorods	85
6.3.2 Characterization of Hydrothermally Grown ZnO Nanorods	86
6.3.2.1 Cathodoluminescence	86
6.3.2.2 Photoluminescence	86
6.3.2.3 X-ray Absorption Near Edge Spectroscopy (XANES)	87
6.3.2.4 Electron Spin Resonance	87

CONTENTS (cont.)

	Page
6.4 Results and Discussion	87
6.5 Conclusions	99
CHAPTER VII CONCLUSIONS	100
REFERENCES	102

LIST OF PUBLICATIONS

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.

S. Anantachaisilp, S.M. Smith, C. Ton-That, T. Osotchan, A.R. Moon, M.R. Phillips, Tailoring Deep Level Surface Defects in ZnO Nanorods for High Sensitivity Ammonia Gas Sensing, *The Journal of Physical Chemistry C*, **118** (2014) 27150-27156.

Matthew R. Phillips, Suranan Anantachaisilp, Liangchen Zhu, Laurent L. Cheong Lem, Christian Nenstiel, Siwaporn Meejoo Smith, Cuong Ton-That, Axel Hoffmann, Visible Luminescence in Bulk and Nanostructured ZnO (Invited Paper), *2014 SPIE Photonics West*, San Francisco, California, USA. February 1–6, 2014.

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S. Anantachaisilp, S.M. Smith, C. Ton-That, T. Osotchan, A.R. Moon, M.R. Phillips, ZnO Nanowires with Enhanced Sensitivity for Ammonia Gas Sensing at Room temperature by Regulating Deep Level Surface Defects. *2014 MATERIALS RESEARCH SOCIETY Fall Meeting & Exhibit*, Boston, Massachusetts. November 30-December 5, 2014.

Matthew Phillips, Suranan Anantachaisilp, Liangchen Zhu, Christian Nenstiel, Nadja Jankowski, Siwaporn Meejoo Smith, Cuong Ton-That and Axel Hoffmann, Chemical Origin of Red Luminescence in Zn. *8th International Workshop on Zinc Oxide and Related Materials*, Niagara Falls, Ontario, Canada. September 8 - 11, 2014.

LIST OF TABLES

Table	Page
1.1 Summary of ammonia gas sensor applications Taken from Timmer <i>et al.</i>	3
2.1 General physical and chemical properties of ZnO	6
2.2 Bound exciton peak energies (eV) in ZnO	24
2.3 Summary of hydrothermal growth of ZnO nanostructures and their morphology	36
3.1 List of Chemicals	38
3.2 List of Instruments	39
5.1 The relative percentage of the integrated intensity of the O _I , O _{II} and O _{III} peaks from the O1s XPS emission for the as-grown, Zn annealed and O ₂ annealed specimens.	77

LIST OF FIGURES

Figures	Page	
2.1	Unit cells of ZnO crystal structures: (a) cubic rocksalt (B1), (b) cubic zinc blende (B3), and (c) hexagonal wurtzite (B4). Zn atoms are represented in gray whereas O atoms are represented in black.	8
2.2	(a) The calculation of ZnO band structure using the HSE hybrid functional. The valence-band maximum energy is at zero. (b) Hexagonal ZnO band structure and symmetries. The valence band splits into three sub-bands; A, B, and C resulting from the effects of crystal-field splitting and spin-orbit coupling.	9
2.3	Illustration of point defects in ZnO crystal structures: (a) Zinc vacancy V_{Zn} , (b) Oxygen vacancy V_O , (c) Zinc interstitial Zn_i , (d) Oxygen interstitial O_i , (e) Zinc antisite Zn_O , (f) Oxygen antisite O_{Zn} and (g) Substitutional impurity at a zinc site e.g. Li_{Zn} , Cu_{Zn} or Al_{Zn} .	12
2.4	Calculated defect formation energy for ZnO native point defects in (a) Zinc-rich conditions and (b) Oxygen-rich conditions.	13
2.5	Calculated ZnO native point defects formation energies as a function of Fermi-level position in both Zn-rich (left) and O-rich (right) conditions. Valence band maximum locates at the zero of Fermi level. Different slope represents different charge state.	18
2.6	Thermodynamic transition levels for ZnO native point defects.	19
2.7	Characteristic ZnO luminescence spectrum presenting the near band edge peak (NBE) and the broad deep level emission (DL).	21
2.8	Schematic diagram of the radiative recombination mechanisms.	23
2.9	Characteristic current-time sensing peak of ZnO nanorods annealed in O ₂ atmosphere response to ammonia gas.	30
2.10	Schematic diagram of oxygen adsorption on the ZnO surface; n = 1 or 2 and s = 1 or 2. (Adapted from Kim <i>et al.</i>)	32

LIST OF FIGURES (cont.)

Figures	Page
2.11 Schematic diagram of the oxidative gas sensing mechanism on ZnO surface. (Green area is the depletion layer.)	33
2.12 Schematic diagram of the reductive gas sensing mechanism on ZnO surface. (Green area is the depletion layer.)	33
2.13 Schematic diagram of ammonia gas sensing mechanism on the ZnO surface; $n = 1$ or 2 and $s = 1$ or 2 .	34
3.1 Photograph of Teflon Lined Autoclave used as a reactor in hydrothermal growth.	40
3.2 Photograph of Lindberg Blue Mini-mite Tube Furnace.	41
3.3 Photograph of plasma chamber showing the overall setup.	42
3.4 Penetration range of the primary electron beam with the origin of electrons, x-rays and light.	43
3.5 Schematic of CL experimental setup.	45
3.6 (a) Twelve fingers of the interdigitated electrode (shown in gray). (b) Gas sensor device comprised of ZnO sensing layer (light gray square), aluminum electrodes (gray), polycarbonate board (outermost square) with conduction line (black line), and connection wires (black dot).	50
3.7 Gas flow controller unit diagram; input channels are shown in dash lines and output channels are shown in solid lines.	51
3.8 Homebuilt gas measurement system; dot line represents shortcut path when the dry measurement starts.	52

LIST OF FIGURES (cont.)

Figures	Page
4.1	(a) SEM images of as-grown ZnO (0001) nanorods on a sapphire substrate and (b) PXRD patterns of as-grown, O ₂ and Zn atmosphere annealed ZnO nanorods exhibiting the wurtzite crystal structure. The change in the relative intensity of the diffraction peaks arises from a slight reorientation of the nanorods relative to the substrate after thermal annealing. 57
4.2	SEM images of ZnO nanorods after annealing in (a) O ₂ and (b) Zn atmosphere. 58
4.3	(a) Normalized CL spectra collected from Zn annealed, as-grown, and O ₂ atmosphere annealed ZnO nanorods at 5 kV, 80 K, scan area = 50 μm × 43 μm, and beam current of 0.2 ± 0.02 nA. The ratio of raw intensities of GL, YL, and RL centered at 2.44, 1.90, and 1.70 eV, respectively, is 0.057:0.204:1. All spectra were normalized to the DL peaks. (b) Room temperature I–V characteristics of the Zn annealed, as-grown, and O ₂ atmosphere annealed ZnO nanorods measured under an ambient atmosphere. 59
4.4	N K-edge XANES spectra of Nitrogen implanted ZnO crystal and ZnO nanoparticles, and as grown, O ₂ , and Zn atmosphere annealed ZnO nanorods. 61
4.5	CL spectra collected from O ₂ atmosphere annealed and H plasma of O ₂ annealed ZnO nanorods at 5kV, 80K. The spectra were normalized to the maximum intensity peaks. 62
4.6	Room temperature <i>I-V</i> characteristic of the Argon atmosphere annealed ZnO nanorod gas sensor. 64

LIST OF FIGURES (cont.)

Figures	Page
<p>4.7 Sensitivity as a function of measurement time for (a) as-grown, (c) O₂, (e) Zn, and (g) H plasma after O₂ annealed ZnO nanorod sensors and sensitivity as a function of ammonia gas concentration for (b) as-grown, (d) O₂, (f) Zn, and (h) H plasma after O₂ annealed ZnO nanorods sensors at room temperature. Labels in the bottom right corner of (b), (d), (f), and (h) indicate the signature luminescence (YL, RL, GL, and RL suppression) exhibited by ZnO nanorods employed in the fabrication of each gas sensor.</p>	65
<p>5.1 SEM images of the as-grown hydrothermal ZnO nanorod ensemble containing a high density of uniform hexagonal <0001> nanorods 50 ± 5 nm in diameter. The oblique nanorod growth habit promotes multiple contact of the sidewalls providing good electrical conductivity across the ensemble.</p>	71
<p>5.2 Typical 5 kV CL spectra collected from as-grown, O₂ atmosphere and Zn vapor annealed ZnO nanorods at 80K, a scan area = 50 μm x 43 μm and beam current of 0.2±0.02nA, showing yellow (YL) at 1.90 eV, green (YL) at 2.44 eV and red (RL) at 1.70 eV.</p>	72
<p>5.3 presents a log I vs log V showing the 1000x and 100x increase in the measured current after Zn vapor and O₂ annealing respectively.</p>	73
<p>5.4 (a) ESR spectra of the as-grown and O₂ annealed ZnO nanorods. Two main paramagnetic ESR signals at g ≅ 2.01 and 1.96 are assigned to singly ionized surface oxygen vacancy defects and localized donors, respectively. (b) ESR spectrum following Zn vapor annealing showing a significant intensity increase in g ≅ 2.00 line after the appearance of a broad green CL emission centered at 2.44 eV and a pronounced shoulder in the valence band photoemission spectrum ~ 3 eV below the Fermi level.</p>	74

LIST OF FIGURES (cont.)

Figures	Page
5.5 The O1s XPS spectra for YL, RL and GL ZnO nanorod samples are shown in Figures 5.5(a), 5.5(b) and 5.5(c) respectively. The XPS profiles are all curve fitted into three peaks at 530.5 eV (Peak O _I), 532.0 eV (Peak O _{II}) and 532.7 eV (Peak O _{III}). Peak O _I results from O ²⁻ ions fully coordinated by Zn and O atoms in the fully stoichiometric wurtzite crystal structure, peak O _{II} is due to either O ²⁻ ions in the vicinity of V _O defects and peak O _{III} arises from oxygen in strongly bound adsorbed gases, specifically H ₂ O and O ₂ molecules.	76
5.6 Valence band X-ray Photoemission Spectroscopy (VB-XPS) spectra taken from the as-grown, O ₂ anneal and Zn vapor anneal ZnO nanorod samples are presented in Figure. 5.6(a). The VB-XPS spectra for all three samples consist of two dominant near edge peaks one centered at ~ 5 eV ascribed to O 2p related states the other ~ 7 eV attributed to hybridized Zn 4s + O 2p states. The leading edge of the valence band photoemission showing the pronounced shoulder around 3 eV below the Fermi level that forms after Zn vapour annealing is shown in Figure 5.6(b).	80
5.7 Downward band bending on the as-grown ZnO nanorod due to electron accumulation and its decrease following O ₂ annealing using the valence band photoemission spectroscopy results in Figure 5.6 (a) and 5.6 (b).	81
5.8 Comparison of continuous-wave 532 and 405 nm sub band gap laser excitation PL spectra at 300 K for ZnO nanorods as-grown and annealed in O ₂ gas. The sub band gap excited spectra reveal a common broad OL emission at 1.95 eV except for the O ₂ annealed sample illuminated with blue light which emits a broad RL around 1.83 eV indicated a different defect structure.	82

LIST OF FIGURES (cont.)

Figures	Page
6.1 SEM image of the as-grown <0001> ZnO nanorod ensemble, showing that the low temperature hydrothermal growth treatment produced a high density of uniform hexagonal <0001> nanorods approximately 55 nm in diameter orientated at different angles to the normal direction of the substrate.	88
6.2 Typical cathodoluminescence spectra collected with 5 kV, $I_B = 0.2 \pm 0.02$ nA and scan area = 50 $\mu\text{m} \times 43 \mu\text{m}$. Fig 6.2a ZnO nanorods before (“as-grown”) and after annealing at 650 °C in O ₂ gas for 30 minutes, showing the creation of the red luminescence (RL) peak centered at 1.78 eV with a FWHM = 0.69 eV. Fig 6.2b illustrates rapid quenching of the RL following exposure to a mild hydrogen plasma indicating that the RL relates to an acceptor-like center as hydrogen is a donor in ZnO. Fig 6.2c. RL spectrum at 15 K showing the peak red shifted to 1.69 eV and narrowing of the FWHM to 0.57 eV. The assignment of the RL to transition metal impurities is ruled out because of the absence of fine structure arising from internal 3d transitions.	90
6.3 Normalized RL intensity versus excitation power (5 kV x I_B) at 80 K (a) and 300 K (b). The absence of a blue peak shift with increasing beam current eliminates the assignment of the RL to donor acceptor pair recombination transitions.	91
6.4 Plot of log (I_{CL}) versus log (I_B) at 80 K (a) and 300 K (b) with I_B in nA. The gradient, n, is the power law exponent in the relationship, $I_{CL} \propto I_B^n$. The $n_{NBE} \sim 1$ is expected for excitonic recombination. The $n_{RL} \sim 0.8$ is higher than expected for a lattice coupled defect most likely due to a high concentration of RL centers.	92

LIST OF FIGURES (cont.)

Figures	Page
<p>6.5 CL intensity versus temperature at 80 K for the RL (a) and NBE (b) with 300 K with 5 kV, $I_B = 0.2 \pm 0.02$ nA and scan area = $50 \mu\text{m} \times 43 \mu\text{m}$. The red shift and narrowing of the RL with decreasing temperature is consistent with configuration coordinate model for radiative recombination. The blue shift and appearance of phonon replicas as the temperature approaches 93 K is expected for excitonic emission with the bandgap shrinkage. The intensity of the RL and NBE exhibits “negative” thermal quenching with increasing temperature.</p>	94
<p>6.6 The plot of the RL peak position and peak width as a function of temperature are shown in Figure 6.6a and Figure 6.6b. Figure 5.6c displays the RL intensity dependence on temperature. With decreasing temperature from 300 K to 93 K a typical thermal response relationship with an activation energy of $E_A = 78.8$ meV is found. However, increasing the temperature from 93 K to 300 K “negative” thermal quenching is observed arising from the presence of shallow levels that fill with carriers at low temperature during electron beam excitation and depopulate with rising temperature increasing the luminescence intensity.</p>	96
<p>6.7 CL spectra at 80 K of the NBE and RL before and after thermal annealing in O_2 are shown in Figure 6.7a with corresponding CL spectra in Figure 6.7b. Figure 6.7a reveals emission due to donor bound exciton around 3.36 eV and peaks at 3.32 and 3.26 eV ascribed to the presence of acceptors in either DAP or free-to-bound transitions. No interrelationship between the 3.32 and 3.26 eV NBE peaks and the RL in the CL spectra is observed. Additionally there is no correlation between the free-to-bound NBE and RL peaks and nitrogen as confirmed in the $\text{N } k\alpha$ XANES results in Figure 6.9.</p>	97

LIST OF FIGURES (cont.)

Figures		Page
6.8	The temperature dependence of the D°X and peaks at 3.32 and 3.26 eV are shown in Figure 6.8. The data show the usual red shift of the D°X with increasing temperature as the band gap widens due to lattice expansion and the electron-phonon effect. The absence of a corresponding shift of the 3.32 and 3.26 eV peaks between 7 and 100 K indicates that free carriers are involved in the recombination process providing thermal energy (k_bT) which offsets the band gap red shift. This result suggests that these emission peaks arise from free-to-bound transition rather than a DAP recombination process.	98
6.9	XANES spectra around the N energy from the “as-grown” and O ₂ annealed samples, as well as from ZnO nano-particles implanted with nitrogen, are shown in Figure 6.9. The results show that no nitrogen is present in both the “as-grown” and O ₂ annealed samples.	99

LIST OF SCHEMES

Schemes	Page
4.1 The alteration of the ZnO Fermi level position owing to near surface acceptor and donor	66

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
<i>S</i>	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