University of the Witwatersrand PhD Degrees by Research thesis examinations
Response to Examiners' Reports

Candidate name	KAO MAHALIEO
Person number	0506670H
Thesis title	Group III-nitrides: Synthesis and sensor applications
Degree	Doctor of Philosophy
School	School of Chemistry
Date	

I confirm that the following amendments have been made to this thesis in light of the examiners' reports, and I consider that the thesis is now satisfactory for the award of the degree.

Supervisor (name)	Prof. Neil Coville		
Signature		**Date**	
Head of School or nominee (name)	Prof Dean Brady		
Signature		**Date**	

Examiner	Examiner's comment	Response	Location or page in revised thesis
1	The nitrides were achieved by using the difficult to handle gases such as ammonia and dangerous UV-sources	All standard safety measures were taken in handling the gas and using the UV source such as: a gas line system made of corrosion resistant material was installed to prevent leakages and a digital flow meter to control gas flow. A dark fume hood space sealed in aluminium foil was used to prevent UV exposure	
1	In chapter 2: The gas sensing technique description if too brief it needs to be beefed up.	The description has been elaborated in chapter 2 and further provided with images in chapter 6 which deals with sensor work	Pg36
	In Chapter 3: While it is well known that the vapor-liquid-solid	The objective of the study was to prepare Group III-nitrides from	Chapter 3: Pg39,45,

	mechanism is responsible for the growth of the nanowires of these oxides; i. The chapter shows weakness in the TEM characterization of the nanowires as there was no attempt to present higher resolution images or electron diffraction pattern to decipher the lattice parameters and the general orientation of the crystal planes of the nanowires. ii. The so-called nano-nails could in fact be nanowires with a blob at the end which is evidence of VLS mechanism of growth where the blob is regarded as the catalyst from which the growing nanowire originates. The so-called nano-necklaces which are normally called nanobeads could be nanocrystals which align with the growing nanowire and which could also be further catalysts which continue linear growth or branched/hierarchical growth.	their oxides. The one dimensional (1D) structures of indium oxide reported in Chapter 3 resulted from an unfortunate experimental procedure that failed to produce nitrides but the positive side was that it converted the three dimensional (3D) indium oxide micro-particles into 1D nanowires of indium oxide. Giving change in size and dimensionality; from micro to nano and from 3D to 1D. Therefore we felt it was important to report on it as a method of micro-machining via CVD which provides a cheaper alternative of top-down approach in comparison to the expensive top-down techniques such as Optical lithography which uses laser and X-ray sources or complex chemical routes such as templated etching, selective dealloying and anisotropic dissolution. i. The study did not expand its resources to cover expensive characterization techniques such as HRTEM. However this has recreated a platform for future studies in this area. ii. The examiner is correct "nano-nails" are in fact nanowires with a catalyst droplet at the top and were previously confirmed by Lao et al. [1] In fact the mechanism presented on page 49 of the thesis indicates what the examiner suggests. They have been named so because of their nail-like appearance.	48 & 49
1	Chapter 4: i. In this Chapter why are all figures and tables at the end of the chapter?	i. The chapter has been fixed to include figures and tables within text to meet the format of the rest of the chapters in this thesis.	Chapter 4

	ii. TEM is still low resolution without lattice fringes and without electron diffraction patterns to confirm the spacing between the atomic planes.	ii. HRTEM was attempted for the InN structures however the quality was poor due to **sample charging** as a result samples were literally shifting across the screen making it impossible to captures crisp lattice fringes. Charging is produced by a build-up of electrons in the sample and their uncontrolled discharge, and can produce unwanted artefacts, particularly in electron images. It causes a range of unusual effects such as abnormal contrast and image deformation and shift.	
	iii. For DRS, there is no explanation on how the Tauc plot is obtained from these DRS data. What is the scattering coefficient values for these materials which was used to obtain the Tauc plot from DRS data?	iii. A series of equations has been added to indicate how the bandgap is derived from the DRS data. The UV-Vis absorption spectroscopy is frequently used to characterize semiconductors thin films. [2] Due to low scattering in solid films, it is easy to extract the Eg values from their absorption spectra knowing their thickness. However, in powdered samples, the scattering effect is enhanced since more superficial area is exposed to the light beam. In normal incidence mode, dispersed light is counted as absorbed light and the technique (optical absorption) does not distinguish between the two phenomena. On the other hand, it is common to obtain powdered samples instead of thin films and frequently UV-Vis absorption spectroscopy is	Pg91-92[5, 6]

		carried out dispersing the sample in liquid media like water, ethanol or methanol. If the particle size of the sample is not small enough, it precipitates and the absorption spectrum is even more difficult to interpret. In order to avoid these complications, it is desirable to use DRS, which enables to obtain Eg of un-supported materials.[3, 4]	
1	In Chapter 5: The candidate presents results on the characterization of In-Ga-N-O systems obtained. I. There still some figures outside the main text of the thesis. II. Also TEM is still low resolution At least one sample can be taken for HRTEM to show lattice spacing and present its electron diffraction pattern of the same to confirm such spacing	I. Figures have been moved within the main text. II. With both rods and plates being porous measuring lattice spacing would only add minimal value to the content as XRD was used to match the crystal system and WDS/EPMA gave elemental analysis of the material.	Chapter 5
1	In chapter 6: Inclusion of the gas concentration plots should be encouraged to see what happens to the response curve at the time of switching ON and OFF of the analyte gas. This is important in deciding what mechanism of detection is at play	A graph of CO gas concentration plot at 250 °C has been added to show overall how the sensor responds at the time the gas is switched On and OFF. Also figures have been moved inside the text.	Pg141
2	Please discuss the significance of the inset of Fig 3.9	Discussed on page 49 last paragraph and amended the caption on page 52	Pg49 & 52
2	No caption is given to Fig. 3.10 (d-f) and fig 3.11 (c-d) please include the appropriate captions for these "forgotten" figures	Corrected	Pg58
2	In regard to section 3.3.2, The candidate refers to the segregation of In_2O_3 to form In metal, the feasibility of this argument against the backdrop of the stable crystal structure of In_2O_3 makes it untenable, In the event of indium formation from In_2O_3, it would mean	It should be taken in to consideration that 99 % NH_3 is highly reducing hence the conversion of $In_2O_3 \rightarrow In_2O \rightarrow In$ is not unexpected, even if not all of the oxide is reduced completely. Now In_2O is known to be unstable and to exist in vapour form, so in	Pg49-50

	that a phase transition occurs or a defective In_2O_3 structure is formed, but this is not supported by the XRD patterns could the candidate reconcile this, I suppose that there could a supersaturation of In	the event that InO was formed in an open CVD system used it would be flushed out of the system and only the stable form In_2O_3 would be collected. While some of the metallic indium was collected outside the reaction zone, some of it settled in the boat and became part of the product. Some of the large solidified indium droplets were visible to the eye and could be separated but some could not and they were picked up by XRD. The XRD pattern of the original (as-purchased) In_2O_3 nicely matched to the XRD patterns of In_2O_3 collected after the reaction and the EVA software identified and matched it to cubic In_2O_3 pattern.	
2	Pg 56 it is indicated that (Figure 3.10) nanowires are formed however the SEM image points a completely different picture as structures with diameters in the order of microns are adduced; this is an anomaly that requires clarification.	Corrected to just wires and tubes/microtubes first paragraph page 56	Pg56 & 58
2	Pg 60 the amount of carbon is insensitive to In_2O_3:C ratio for ratios lower than 3:1, how do you reconcile the fact that the 1 :0 ratio has a larger C intensity compared to the 2: 1 and 1: 1 respectively	The carbon content in the EDS spectrum cannot be a reflection of the carbon in the product as each sample is coated with a carbon coat before it was viewed under SEM to reduce sample charging. However if there was a significant amount of the carbon in the product itself XRD patterns in pages 65-67 would have showed its presence.	Pg60,65-67
2	In Fig. 3 .13 the candidate presents a comparative argument on the peak intensities of the oxide, however the figure presents the intensity in a.u., hence any attempts at comparison are difficult as no absolute intensity values have been given	Corrected, absolute intensity values provided on the graph Fig.3.13.	chapter3 Pg65
2	Pg 65: The XRD pattern does not surely belong to a In_2O_3 system, this seems like a superstructure or a low symmetry system, I presume the candidate implied the pattern of $In_3(PO_4)_2$	To eliminate the confusion the figure caption has been changed from “XRD patterns of samples prepared from…” to “XRD patterns of $In_3(PO_4)_2$ samples prepared from….”	Pg65 & 66

2	Pg 68: The candidate should consider the solubility limits of C in the metal and also thermodynamic arguments such as bond enthalpy of In-C and In-O to explore the mechanism of nanostructure formation in C environment	With the starting materials being In_2O_3 and carbon it is highly unlikely that indium would exchange O for C as the In-O bond is more stable than the In-C. Rather as indicated by Yin et al. and references within this is the most likely route and XRD patterns show the formation of metallic indium as by-product. $In_2O_3 + C \rightarrow In_2O + CO \rightarrow In + CO_2$.[7] In the event that gaseous carbon dissolved in the formed indium droplets, carbon structures would be expected to grow from these In droplets, which is NOT the case here.	Pg68
2	Pg 75: The role of intensity of the UV source was not established, ideally the influence of a light source, the pulse duration are essential parameters that determine the nature of the structures formed, their dispersity and yield, could the candidate state why this was not considered as a significant experimental parameter and possibly consider it for future outlook. More comments provided in Pg 75	Mercury UV-lamps emit a range of energies of varying intensity. Future studies using a Laser source which can produce a specific wavelength would be necessary to investigate the intensity of the UV source.	Pg75
2	Pg 77, How does the candidate distinguish In_2O_3 and InN from a mere microscopy image, given that both compounds have large array of possible (nano) structures that can be formed?	The microscopy images of In_2O_3 were taken from as-purchased In_2O_3 prior to synthesis, thus the candidate was able to establish a morphological transformation after the reaction by comparing the starting material and the end product in TEM and SEM images supported by XRD qualitative analysis.	Pg80
2	The candidate has used XRD to establish the purity of InN nanostructures however this technique is inherently insensitive to low scatter volumes, amorphous phases and material content thus a complementary technique such as Raman could be considered, a comparison between the LO and TO modes specific to InN and In_2O_3 could yield suitable and reliable data.	The Raman modes of the InN tubes have been investigated in the study (pg 90) and they agree with the literature values reported and established for InN and are therefore in agreement with the XRD pattern.	Pg85 & 90

2	It is not clear why the candidate has used in Pg 80 the bulk values of the strain free InN to proclaim the existence of stress/ strain in the InN nanostructures, why was the effect of quantum confinement not considered and similarly for self -consistency the strain value could have been compared to that determined by XRD (lattice parameter change)	The average diameter of the InN tubes is 30-40 nm which rules out quantum confinement as the reason for the slight shift in Raman modes but rather defects are more likely to be responsible. Quantum confinement is a significant parameter for diameters less than 5 nm.	
2	It is not clear to me why the Burstein -Moss effect is considered for InN yet it has a high band gap of -2.0eV, indeed this effect is predominantly observed under the following conditions: i) Low effect mass (mainly n-type semiconductors) ii) Low density of states in the conduction band that preclude inter-band transitions to the low lying states of the CB. iii) A small band gap.	The Moss-Burstein effect is one of the long standing theories in InN studies used to explain the observation of the higher band gap value.	Chapter 1 Pg14
2	In pg 83, the candidate refers to InN as being pure yet there are traces of In therein. Please give clarity to the statement	The statement is based on the quality of InN in the XRD pattern in Fig. 4.7.	Pg85
2	Table 4.1 please elaborate on whether the XRD column is a qualitative observation or quantitative, a supplementary technique is needed for cases in which InN is amorphous.	XRD is largely a qualitative technique hence the data tabulated from it.	Pg76
2	Fig 4.12, Were Penni-golden rules for the transitions used and hence what form of inter-band transition was established, direct allowed transition or direct forbidden or indirect allowed transitions. A clarification would be helpful for comprehensive understanding.	It has been established in the literature that wurtzite InN and GaN are direct bandgap materials and while the band gap value of InN maybe still be a subject of the debate the type of transitions are however agreed upon as direct.	Chapter 4 pg92
2	Fig. 4.13, it is essential that the substrate is explicitly stated since the interfacial energies will determine whether In wets the substrate or not ... refer to Pg 93 for more elaboration	Pg 95 It is stated that the quartz boat was used and the fluffy end product was collected from the quartz boat.	Pg95
2	Pg 113, It is noted that the growth of GaN nanostructures is determined	Pg 113 Fig.5.2 showed 1D structures of as-purchased Ga_2O_3	

	by i) 2D nucleation in the absence of an asymmetric step barrier ii) Ehrlich - Schwebel Barrier (ESB) height which favors the formation of lD nanostructures, there is no mention in the text on the contributions of these factors in regard to the nanostructures formed.	and Fig. 5.3 -5.5 show the 1D GaN structures similar to the precursor suggesting no morphological transformation. However Fig.5.6 shows that 2D GaN structures formed from what was 1D Ga_2O_3 hence the study considered only the 2D nucleation process because in reality 1D structures were not formed in this study. They were bought from Sigma already as 1D.	
2	Pg 117, please address the suggestion presented in this page particularly on the issue of the absence of In in the WDS data	Pg 117-119 the EDS and WDS spectra and the EPMA table all show the presence of In with an average atomic percentage of 0.17 hence the low intensity of the In peak on the EDS spectrum on pg 117.	Pg117-119
2	Pg 120, it is not clear where the issue of lattice mismatch arises from as the growth of InGaN is not carried out on a GaN substrate, clarity needed to qualify the validity of the argument	The issue of lattice mismatch is not used to account for the results observed in this study but rather cited that some authors used it to explain a blue shift in their InGaN PL results. This study used defects and stress to explain the observed blue shift in PL.	Pg123-124
2	It is essential that the conditions of the PL measurements are stated especially the temperature at which the measurements were carried out.	Amended. Modified Raman and PL measurements were done at room temperature.	Pg111
2	Chapter 6: This chapter presents a very important finding on the possible application of InN and GaN as CO sensors, indeed the articulation of the results is excellent, however more data mining can be carried out in this chapter in regard to the following sensor benchmarks: i) Dynamical range, ii) Hysteresis, iii) Sensor stability, iv) Linearity and recovery time.	I. The lowest studied concentration was 5 ppm and the highest 100 ppm and thus provides the set dynamic range for this study. However with the saturation limit changing with the analyte and temperature the set dynamic range is reduced and varies. (Fig. 6.2 - 6.6) II. The advantage of using a flow through method in the sensor experiments is that the sensor response can be recorded repeatedly pg 168 III. Repetitive cycles at different temperatures show sensor stability IV. Linear and non-linear	Chapter 6

		responses as well recovery times are shown in Fig. 6.7 & 6.8 on pages 156 &159	
3	How InN nanobelts are stable up to 800 °C when InN is reported to disintegrate >650 °C	Several studies have reported synthesis of InN above 650 °C. This is where experimental data differs from theoretical calculations.	Chapter 4
3	Why the band gap of lnN nanostructures are found to be high (1.89, and 2.19 e V) when literature reports it to be < I e V	The InN band gap has two reported values under debate the high value and the low value. Chapter one deals with the literature of these values.	Chapter 4
3	How do you ensure that emission peat at 2.86 eV is due to the formation of InGaN and not due to the detect states in GaN	It would suggest that the defects states in InGaN (2.8 eV) are different from those in GaN (3.2 eV) which would in turn mean the presence of In is responsible for such defects.	Chapter 5 Pg125
3	What is the selectivity of these materials (lnN, GaN, and In_2O_3) towards CO, NH_3, CH_4 and NO_2 gases?	InN favours CO at 250 °C [Fig. 6.2], GaN favours CH_4 at 300 [Fig. 6.6]and SnO_2 favours NH_3 at 350 °C [Fig. 6.3]	Chapter 6 Pg142-154

References

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