# Theoretical and Experimental Studies of ZnO Nanowires Grown by Vapour Phase Transport

by

## Ruth B. Saunders B. Sc., M. Sc.

A thesis submitted to Dublin City University

for the degree of

Doctor of Philosophy

Research Supervisor

Dr. Enda McGlynn

May, 2012

## Declaration

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of Doctor of Philosophy is entirely my own work, that I have exercised reasonable care to ensure that the work is original, and does not to the best of my knowledge breach any law of copyright, and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

Signed:

ID No.: <u>96495294</u>

Date:

### Acknowledgements

Firstly, I would like to thank my supervisor, Dr. Enda McGlynn, for giving me the opportunity to work with him on such an interesting project. It has been a privilege and I have benefited greatly from his support, ideas, reassurance, understanding and guidance.

I am also indebted to several members of staff both in DCU and further afield. I am very grateful to Jonas Johansson from Lund University, Sweden, for his advice and assistance at critical points in my research. I would also like to thank Prof. Martin Henry for his input and insight into my work. Thank you also to Dr. Tony Cafolla for always taking time to chat and give advice about Physics, books and tv shows. I must thank all the staff at DCU, in particular Lisa Peyton, Sheila Boughton, Patricia James, Sarah Hayes and Alan Hughes, for the help they have given me during my doctoral studies.

I want to express my gratitude to all my colleagues at DCU: Dr. Daragh Byrne, for readily sharing his extensive knowledge and for answering my every question; Seamus Garry, for his endless generosity, kindness and patience; and Dr. Mahua Biswas, Ciaran Gray and Joseph Cullen for their help and input.

Thank you too to the friends who have enriched my experience at DCU; my office mates Dr. Conor McLoughlin, Dr. Paddy Kavanagh and especially Dr. Mairead Hurley, who girled up the office and shared many crafty chats; the denizens of S109a for their providing great support, positivity and comic relief: Conor Coyle, Colm Fallon, Eanna McCarthy, Mossy Kelly, Seamus Garry, Nicky Walsh and Jiang Xi; Catherine Doyle for long conversations, keeping me up to date with good television and knitting breaks; Dr. Christy Charlton for knowing exactly when to suggest a tea break.

I want to express my deep appreciation for the friends and family who have helped me so much throughout my studies: to Penny and Evan Salholm for good food, good cheer and support; to my mother, Ann, for her enthusiasm and encouragement; to my friends Conor, Gillian, Gail and Jennifer; to Ben Crane for being my yoga buddy and a beacon of calm; to Fiona and Simon - my very first Physics friends and colleagues in DCU, so many years ago - for helping me through exams and dramas and offering unwavering support and friendship; to Colleen, for taking me under her wing, translating for me, teaching me a lot of Physics, drinking a lot of tea, and hosting summit meetings and tarot card readings, as the occasion demanded.

I would like give special thanks to my brother, Karl, who introduced me to Physics with a riveting explanation of sound waves and echoes when I was eleven, and to my sister-in-law, Ruzena, for her kind encouragement. To my sister Astrid (and to Brian!), thank you for enduring many long-winded explanations of Physics and being with me every step of the way. To my godmother, Christina Albertini, thank you for believing in me always and remaining my greatest champion. To Vivienne Gaynor, thanks for sharing many years of laughter and confidences and for her readiness to fight my corner.

Finally, I would like to acknowledge the kindness and support of my wonderful husband Erik, whose chuckles have brightened my life immeasurably. To my lovely husband, Erik.

### Abstract

This thesis discusses the growth atmosphere, condensing species and nucleation conditions relevant to vapour phase transport growth of ZnO nanowires. The partial pressure of molecular ZnO in a Zn/O2 mix at normal ZnO growth temperatures is  $\sim 6 \times 10^{-7}$  of the Zn partial pressures. In typical vapour phase transport growth conditions, using carbothermal reduction, the Zn vapour is always undersaturated while the ZnO vapour is always supersaturated. In the case of the ZnO vapour, our analysis suggests that the barrier to nucleation is too large for nucleation of ZnO to take place, which is consistent with experimental evidence that nanostructures will not grow on unseeded areas of substrates. In the presence of suitable accommodation sites, due to ZnO seeds, growth can occur via Zn vapour condensation (followed by oxidation) and via direct condensation of molecular ZnO. The balance between these two condensing species is likely to be a sensitive function of growth parameters. This thesis also examines the relationship between the length and radius of ZnO nanowires grown via VPT and finds that the lengths of the nanowires increase with decreasing radius, supporting the inclusion of a diffusion term in a model for the incorporation of molecules into a growing nanowire.

## Contents

1	Intr	duction	1
	1.1	Introduction	1
	1.2	ZnO	2
		1.2.1 Background	2
		1.2.2 ZnO: Material properties	4
		1.2.3 Potential applications of ZnO/ZnO nanostructures	6
	1.3	Thesis motivation	7
	1.4	Thesis outline	9
	Bibl	graphy	11
<b>2</b>	Exp	rimental methods	18
	2.1	Introduction	18
	2.2	Overview of methods for growing ZnO nanowires	18
	2.3	Growth substrate and preparation for ZnO nanowire growth $\ldots$ .	21
		2.3.1 Substrate choice and cleaning	21
		2.3.2 Seed layer choice	22
		2.3.3 Buffer layer deposition	25
	2.4	Vapour phase transport growth of ZnO nanowires	28

		2.4.1	Growth procedure for VPT	29
		2.4.2	Furnace temperature	31
		2.4.3	Growth duration	31
		2.4.4	Oxygen introduction	32
	2.5	Charao	cterisation	34
		2.5.1	Scanning electron microscope imaging	36
		2.5.2	Image analysis	37
	Bibl	iograph	y	38
3	The	ermody	namic analysis of Zn vapour	44
	3.1	Introd	uction	44
	3.2	The G	ibbs free energy of reaction for the carbothermal reduction of	
		ZnO		47
	3.3	The sa	turation of Zn vapour	49
		3.3.1	Calculation of the partial pressure of Zn vapour $\ . \ . \ . \ .$	49
		3.3.2	The degree of saturation of Zn vapour	52
		3.3.3	Alternative definition of the vapour pressure of Zn vapour $\ .$ .	55
	3.4	The in	npingement rate of Zn atoms	57
	3.5	Conclu	sions	59
	Bibl	iograph	y	61
4	The	ermody	namic analysis of ZnO vapour	63
	4.1	Introd	uction	63
	4.2	ZnO g	aseous molecule	64
	4.3	A mod	lel to calculate the Gibbs free energy of a diatomic molecule	66
		4.3.1	Translational contribution to the partition function	68

		4.3.2	Rotational contribution to the partition function	70
		4.3.3	Vibrational contribution to the partition function	72
		4.3.4	Electronic contribution to the partition function	75
		4.3.5	The Gibbs free energy	76
		4.3.6	Testing the model	77
	4.4	Values	s used in model	79
		4.4.1	ZnO gaseous molecule	79
		4.4.2	$O_2$ gaseous molecule $\ldots \ldots \ldots$	80
	4.5	The sa	aturation of ZnO vapour	81
		4.5.1	Calculation of the Gibbs free energy of reaction for the forma-	
			tion of ZnO vapour	81
		4.5.2	Calculation of the partial pressure of ZnO $\ . \ . \ . \ . \ .$	84
		4.5.3	The degree of saturation of ZnO vapour	86
	4.6	The ir	npingement rate of ZnO molecules	87
	4.7	Concl	usions	89
	Bibl	iograph	ıy	90
<b>5</b>	Nuc		n of ZnO	93
	5.1	Introd	luction	93
	5.2	Homo	geneous nucleation of ZnO vapour	96
		5.2.1	Energy barrier to homogeneous ZnO nucleation	96
		5.2.2	Rate of homogeneous nucleation of ZnO	101
	5.3	Hetero	ogeneous nucleation of ZnO vapour	104
		5.3.1	Energy barrier to heterogeneous nucleation of ZnO without	
			lattice mismatch	104

		5.3.2	Energy barrier to heterogeneous nucleation of ZnO including	
			lattice mismatch	107
		5.3.3	Rate of heterogeneous nucleation of ZnO $\ldots$	110
	5.4	Conclu	isions	115
	Bibl	iograph	y	116
6	Rel	ationsh	nip between the length and radii of ZnO nanowires	118
	6.1	Introd	uction	118
	6.2	Model	to calculate the length of a nanowire as a function of nanowire	
		radius		120
		6.2.1	Term 1: Atoms/molecules arriving directly to the top of the	
			nanowire	122
		6.2.2	Term 3: Atoms/molecules diffusing from the substrate to the	
			top of the nanowire	123
		6.2.3	Term 2: Atoms/molecules diffusing from the sidewalls to the	
			top of the nanowire	126
		6.2.4	Model results	128
	6.3	Compa	arison of model to experimental results	132
		6.3.1	ZnO nanowires grown via VPT	133
		6.3.2	ZnO nanowires grown in 2.0 sccm of $O_2$	136
	6.4	Conclu	isions	140
	Bibl	iograph	y	142
7	Con	clusio	ns	145
	7.1	Introd	uction and experimental work	145
	7.2	Therm	nodynamics of the gas atmosphere during VPT growth $\ldots$ .	146

		7.2.1	Further discussion on limitations of model used and of exper-	
			imental set-up	147
	7.3	Nuclea	ation of ZnO	149
	7.4	Growt	h rate of ZnO nanowires	151
	7.5	Conclu	usion	155
	Bibl	iograph	ly	157
$\mathbf{A}$	App	oendix	: MATLAB programs	158
	A.1	MATI	AB program to calculate Gibbs free energy of ZnO	158
	A.2	MATI	AB program to calculate equillibrium constant for ZnO reaction	162
	A.3	MATA	ALB program to calculate the partial pressure of Zn produced	
		by CT	'R	163
	A.4	MATI	LAB program to calculate partial pressure of ZnO	166
	A.5	MATI	LAB programs to calculate vapour pressure of ZnO	168
		A.5.1	To find the vapour pressure of Zn vapour over solid ZnO $$	168
		A.5.2	Using the vapour pressure of Zn vapour, to find the vapour	
			pressure of ZnO	168
	A.6	MATI	LAB program to calculate the degree of saturation of ZnO vapour	170
	A.7	MATI	AB program to calculate rate of homogeneous nucleation	171
	A.8	MATI	AB program to calculate the rate of heterogeneous nucleation .	174
	A.9	MATI	AB program to calculate growth rate and nanowire length as	
		a func	tion of radius	177

# List of Figures

1.1	Number of records returned by a search for 'ZnO nano <sup>*</sup> ' and for 'ZnO	
	$\operatorname{nano}^*$ model growth' or 'ZnO $\operatorname{nano}^*$ theory growth' in ISI Web of	
	Science on $22^{nd}$ of May 2012	3
1.2	Unit cell of Wurtzite structure of ZnO (image taken from [8]). The	
	grey balls represent zinc atoms and the yellow balls represent oxygen	
	atoms	4
1.3	Illustration of the hexagonal ZnO structure showing the $c$ -plane, $a$ -	
	plane and $m$ -plane	5
1.4	Selection of TEM/SEM images of ZnO nanostructures taken from lit-	
	erature (a) nanowalls from Grabowska et al. [30], (b) nanoring from	
	Wang et al. [36], (c)nanoflower from Sun et al. [34], (d) nanonee-	
	dles from Lorenz et al. [35], (e) nanowires grown in our system, (f)	
	nanobelts from Wang <i>et al.</i> [36]	8
2.1	Illustration of the VLS growth mode	23
2.1		20
2.2	ZnO nanowires grown on deposited gold seeds	24
2.3	ZnO nanowires grown on a ZnO buffer layer $\hdots$	25

2.4	Two stages of buffer layer deposition (a) ZnO seed layer (b) Chemical	
	bath deposition ZnO layer	26
2.5	Illustration of ZnO nanowires grown by CTR-VPT on substrates pre-	
	pared with a deposited ZnO buffer layer	29
2.6	Illustration of experimental set up for VPT growth	30
2.7	Furnace temperature as a function of time	31
2.8	Illustration of apparatus to measure the actual $O_2$ gas flow from MFC	34
2.9	Schematic of SEM adapted from [30]	37
3.1	Illustration of the stages of VPT growth of nanostructures $\ . \ . \ .$ .	45
3.2	Possible paths to formation of $ZnO(s)$ :(a)Condensation of Zn vapour	
	and subsequent oxidation to form $ZnO(s)$ , (b)Direct condensation of	
	ZnO vapour to ZnO(s) (adapted from reference [6]) $\ . \ . \ . \ .$ .	46
3.3	Gibbs free energy of reaction for CTR of ZnO as a function of tem-	
	perature	48
3.4	Illustration of the condensation of Zn vapour, ${\rm Zn}(g) \to {\rm Zn}(c)  . \ . \ .$	50
3.5	The partial pressure and vapour pressure of Zn vapour produced by	
	the CTR of ZnO powder as a function of temperature	51
3.6	Degree of saturation for $\operatorname{Zn}(g)$ over condensed phase Zn as a function	
	of temperature	54
3.7	SEM image of nanostructure growth showing no growth on bare/unseeded	ł
	$\rm Si/SiO_2$ substrate $\ldots$	55
3.8	Illustration of reaction $ZnO(s) \rightarrow Zn(g) + \frac{1}{2}O_2$	56
3.9	The degree of saturation of Zn vapour over solid ZnO as a function	
	of temperature	56

### LIST OF FIGURES

3.10	Effective impingement rates for Zn and $O_2$	59
4.1	Illustration of the formation and condenstation of ${\rm ZnO}(g)$	64
4.2	Potential energy of a diatomic molecule as a function of internuclear	
	distance r: showing equilibrium distance $r_{\rm e},$ dissociation energy $D_0,$	
	and the vibrational energy levels, adapted from $[3]$	65
4.3	A diatomic molecule	68
4.4	Rotational motion of diatomic molecule	70
4.5	Vibrational motion of diatomic molecule	73
4.6	Potential energy of a diatomic molecule approximated as a parabolic	
	function	74
4.7	The Gibbs energy function for $\mathrm{O}_2$ as a function of temperature	78
4.8	The Gibbs energy function for CO as a function of temperature $\ . \ .$ .	78
4.9	$\Delta G_r$ for reaction $Zn(g) + \frac{1}{2}O_2(g) \rightarrow ZnO(g)$ as a function of temperature	83
4.10	Illustration of the evaporation of ZnO	85
4.11	The partial and vapour pressures of ZnO as a function of temperature	86
4.12	The degree of saturation of ZnO vapour as a function of temperature	87
4.13	Effective impingement rates for Zn, $O_2$ and ZnO species as a function	
	of temperature	88
5.1	The general form of the variation of the Gibbs energy for a spherical	
	nucleus as a function of nucleus radius	94
5.2	Nuclei with $\rm r < \rm r_{c}$ will decay. Nuclei with $\rm r > \rm r_{c}$ will continue to grow	95
5.3	Illustration of (a) homogeneously nucleating crystals and (b) hetero-	
	geneously nucleating crystals	96
5.4	Geometry of a homogeneously nucleated ZnO crystal	97

5.5	Energy of homogeneously nucleated ZnO crystal in a supersaturated
	vapour (s = $1.99 \times 10^8$ ) as a function of crystal side length 99
5.6	Energy of homogeneously nucleated ZnO crystal in an undersaturated
	vapour as a function of crystal side length
5.7	Energy barrier to homogeneous nucleation for ZnO nuclei as a func-
	tion of temperature
5.8	Rate of nucleation for homogeneous nucleation of ZnO nuclei as a
	function of temperature
5.9	Illustration of substrate placement showing the available volume of
	vapour
5.10	Geometry of a heterogeneously nucleated ZnO crystal
5.11	Energy barrier to heterogeneous nucleation of ZnO nuclei as a func-
	tion of temperature without lattice mismatch
5.12	Illustration of the lattice mismatch between ZnO and Si 107
5.13	Energy of heterogeneously nucleated ZnO crystal as a function of
	crystal side length
5.14	Energy barrier to heterogeneous nucleation of ZnO as a function of
	temperature
5.15	(a)View from above of adsorbed molecules on the substrate arriving
	at the perimeter of the crystal (b) Molecules arriving at the crystal
	surface area from vapour
5.16	Rate of arrival of molecules ( $\omega_a$ (solid line), $\omega_b$ (dashed line)) to the
	nucleating crystal as a function of temperature
5.17	Rate of nucleation for heterogeneous nucleation of ZnO nuclei as a
	function of temperature

6.1	Illustration of the impingement of molecules on a growing nanowire $~$ . 122 $$
6.2	Schematic of growing nanowire
6.3	Atom/molecule density on the substrate as a function of distance
	from the nanowire
6.4	Nanowire growth rate as a function of time
6.5	Nanowire length as a function of time showing effect of different terms $131$
6.6	Nanowire length as a function of radius
6.7	SEM images of ZnO nanowires grown via general VPT
6.8	Nanowire length as a function of radius for sample with a growth time
	of 30 minutes
6.9	SEM images of ZnO nanowires grown in 2.0 sccm of $O_2$ for 40 minutes 137
6.10	Nanowire length as a function of radius for sample grown for 40 min-
	utes in 2.0 sccm of $O_2$
6.11	SEM images of ZnO nanowires grown in 2.0 sccm of $O_2$ for 20 minutes 139
6.12	Nanowire length as a function of radius for sample grown for 20 min-
	utes in 2.0 sccm of $O_2$
7.1	TEM images (acquired by Rabie Fath Allah, Teresa Ben and David
	Gonzalez Robledo, UCA Cadiz) of ZnO nanowires grown by Dr. Daragh
	Byrne [1]
7.2	ZnO nanowires grown via VPT on spaced nanowire arrays with 1.5
	$\mu m$ spacing, provided by Seamus Garry
7.3	Preliminary measurements of nanowire length as a function of radius
	for ZnO nanowires grown via VPT on spaced nanowire arrays with
	$1.5~\mu m$ spacing, provided by Seamus Garry

7.4	ZnO nanowires grown via VPT showing two different radii, provided	
	by Dr. Daragh Byrne [4]	. 155

# List of Tables

2.1	Comparison between measured gas flow value and value displayed on	
	MFC	34
4.1	Reported values for ZnO molecule	79
4.2	General values for ZnO molecule used in calculations $\hfill\hfil$	80
4.3	Values for $O_2$ molecule used in calculations	81

# List of Acronyms

AFM:	Atomic Force Microscopy
CBD:	Chemical Bath Deposition
CTR:	Carbothermal Reduction
CVD:	Chemical Vapour Deposition
MBE:	Molecular Beam Epitaxy
MFC:	Mass Flow Controller
MOCVD:	Metal Organic Chemical Vapour Deposition
MOVPE:	Metal Organic Vapour Phase Epitaxy
PL:	Photoluminescence
PLD:	Pulsed Laser Deposition
PVD:	Physical Vapour Deposition
SEM:	Scanning Electron Microscopy
TEM:	Transmission Electron Microscopy
VLS:	Vapour Liquid Solid
VPT:	Vapour Phase Transport
VS:	Vapour Solid
XPS:	X-ray Photoelectron Spectroscopy
XRD:	X-ray Diffraction

### Publications

"Length versus radius relationship for ZnO nanowires grown via Vapour Phase Transport", **R. B. Saunders**, S. Garry, D. Byrne M. O. Henry, E. McGlynn *Manuscript in preparation* 

"Theoretical Analysis of Nucleation and Growth of ZnO Nanostructures in Vapour Phase Transport Growth", **R. B. Saunders**, E. McGlynn, M. O. Henry, *Crystal Growth and Design, 2011, 11 (10)* 

"Thermodynamic aspects of the gas atmosphere and growth mechanism in carbothermal vapour phase transport synthesis of ZnO nanostructures", **R. B. Saunders**, E. McGlynn, M. O. Henry, *Thin Solid Films, 2008 518 (16)* 

"Growth of ZnO nanostructures on Au-coated Si: Influence of growth temperature on growth mechanism and morphology", R. T. R Kumar, E. McGlynn, M. Biswas, **R. B. Saunders**, G. Trolliard, B. Soulestin, J. R. Duclere, J. P. Mosnier, M. O. Henry, *Journal of Applied Physics 2008*, 104 (8)

### Presentations

"Modelling the conditions for Nanowire Growth: the Nucleation of ZnO Vapour during Vapour Phase Transport growth", **R.B. Saunders**, E. McGlynn, M.O. Henry, Poster presentation, BOC Poster competition, 3<sup>rd</sup> prize winner, Dublin City University, April 2012,

"Theoretical analysis of nucleation and growth of ZnO nanostructures", **R.B. Saunders**, E. McGlynn, Oral presentation, The Nanometer Structure Consortium at Lund University, Sweden, October 2011

"Theoretical Studies of the Gas Atmosphere Growth Mechanism in Carbothermal Vapour Phase Transport Synthesis of ZnO Nanostructures", **R.B. Saunders**, E. McGlynn, M.O. Henry, Poster presentation, Nanowire Growth Workshop, Rome, November 2010

"ZnO Nanowire Growth: theory and experiment", **R.B. Saunders**, E. McGlynn, M.O. Henry, Oral presentation, LEL Seminar, Dublin City University 2010

"Thermodynamic Aspects of the Gas Atmosphere Growth Mechanism in Carbothermal Vapour Phase Transport Synthesis of ZnO Nanostructures", **R.B. Saunders**, M, Biswas E. McGlynn, M.O. Henry, Poster presentation, EMRS Meeting, Strasbourg, June 2009

### Chapter 1

### Introduction

### 1.1 Introduction

ZnO is a promising semiconducting material with many exciting applications and a strong propensity to grow in nanostructured form. ZnO nanostructures display a wide range of morphologies which are sensitive to growth parameters such as temperature, substrate type and the method used to generate source species. Because of this sensitivity and morphological diversity, a greater theoretical understanding of the growth process is required in order to reproducibly grow specific ZnO nanostructure morphologies, especially on an industrial scale.

A common method of ZnO nanowire growth is vapour phase transport (VPT) using carbothermal reduction (CTR) of ZnO powder by graphite to generate the Zn source species. In this thesis we explore the thermodynamics of the gaseous atmosphere in the VPT process to identify the condensing species during this growth as well as the nucleation conditions. We also present a model for examining the kinetics of nanowire growth which allows us to better understand the growth processes and to predict lengths of ZnO nanowires grown using VPT.

This chapter gives a brief introduction to ZnO as a material, and ZnO nanowires in general and describes the layout of the thesis.

#### 1.2 ZnO

#### 1.2.1 Background

ZnO is a material long known to science and technology. It is reported to have been used in metallurgical processes over 3000 years ago [1] and also played a role in the burgeoning of science during and preceding the Age of Enlightenment. For example, ZnO was known originally to alchemists as 'lana philosophica' or philosopher's wool [2]. Zinc metal was burned in air as part of alchemal rituals and the fluffy white ZnO deposit produced was collected. ZnO also occurs naturally in the earth's crust as the mineral zincite. It has been used for many years and up to the present day as a pigment in paints and enamel coatings and as an ingredient in cements, glass, tires, glue, matches, white ink, reagents, photocopy paper, flame retardant, fungicides, cosmetics and dental cements. There are  $\sim 100,000$  tonnes of ZnO produced per year for such applications [3].

In addition to these common uses, ZnO has been studied as a semiconductor for a long time, with the first demonstration of its semiconducting properties in the 1920s [4]. Improvements in the growth of high quality, single crystalline ZnO in bulk and epitaxial forms led to a peak of interest in research of ZnO in the 1960's. Interest faded when problems with the material, such as difficulties in effectively doping the material p-type became apparent.

The recent period of interest in ZnO was sparked by a variety of factors such as publications reporting optically pumped lasing effects seen in thin films and nanostructures at room temperature [5,6], and the potential of ZnO as a competitor (with intrinsic material advantages, including availability of bulk, single crystal, substrates and a significantly larger exciton binding energy) to GaN [7]. These factors, combined with a surge of interest in nanotechnology, and the fact that ZnO grows naturally in a variety of nanostructured forms, have sustained this research peak for over ten years (as is illustrated in Figure 1.1). Due to its wide range of applications ZnO is the subject of greater than 2,000 peer-reviewed new publications each year.



Figure 1.1: Number of records returned by a search for 'ZnO nano<sup>\*</sup>' and for 'ZnO nano<sup>\*</sup> model growth' or 'ZnO nano<sup>\*</sup> theory growth' in ISI Web of Science on 22<sup>nd</sup> of May 2012.

#### **1.2.2** ZnO: Material properties

ZnO is a II-VI semiconductor material with a wide direct band gap of 3.34 eV [4]. A material with a direct band gap is technologically beneficial, as radiative recombination in an indirect band gap material cannot occur without a change in momentum (to conserve crystal momentum), which normally requires phonon absorption/emission, making it a much lower probability process. The large band gap of 3.34 eV corresponds to light in the blue/UV spectrum, which is again a technologically desirable quality, with applications in lighting, data storage etc. ZnO has an exciton binding energy of 60 meV [4], 2.4 times greater than the thermal energy at room temperature, thus allowing for a more efficient excitonic light emission at room temperature.



Figure 1.2: Unit cell of Wurtzite structure of ZnO (image taken from [8]). The grey balls represent zinc atoms and the yellow balls represent oxygen atoms

ZnO binding in crystal lattice involves an sp<sup>3</sup> hybridization of the electron states. This leads to four equivalent orbitals in a tetrahedral geometry. Molecules with tetrahedral geometry generally form either a zinc-blende crystal structure or a hexagonal wurtzite structure depending on the close-packed layer stacking sequence. The natural crystal structure of ZnO is hexagonal wurtzite, as shown in Figure 1.2. Due to the strong electronegativity of oxygen, the ZnO bond has a considerable degree of polarity. This high polarity is responsible for the occurrence of hexagonal wurtzite over zinc-blende, which tends to occur for lower polarity bonds [3]. This observed preference for hexagonal wurtzite structure has been confirmed theoretically [9].

The wurtzite unit cell contains two ZnO molecules. The lattice parameters are a = b = 0.3249 nm and c = 0.52042 nm [10]. The *c* axis is along the [0001] direction. The volume of one unit cell is  $5.08 \times 10^{-29}$ m<sup>3</sup>. There is a very small deviation in the axis ratio (c/a=1.602) from the ideal close-packed wurtzite axis ratio(c/a=1.633) because of the higher polarity of the ZnO bond [3].



Figure 1.3: Illustration of the hexagonal ZnO structure showing the c-plane, a-plane and m-plane

ZnO is an anisotropic material and thus has different values of surface energy for different faces [4]. Figure 1.3 shows the principal planes of the ZnO wurtzite crystal structure. The *c*-plane consists of alternating positively charged Zn planes (0001) and negatively charged O planes (000-1) with surface energies of 2.0 J/m<sup>2</sup> [11]. The *m*-plane surfaces (10-10) or the side faces of the crystal, which are terminated by both Zn and O atoms are non polar, and the surface energies are 1.15 J/m<sup>2</sup> [11]. The *a*-plane (1-120) is also non polar with a surface energy of 1.25 J/m<sup>2</sup> [12]. This anisotropy is a very important factor in nanostructure growth as it leads to the preferential growth of ZnO along the *c*-axis as there will be preferential atom/molecule incorporation on the polar faces rather than on the side non polar faces.

#### **1.2.3** Potential applications of ZnO/ZnO nanostructures

As mentioned in Section 1.2.2, ZnO is a promising material for blue/UV optoelectronic devices. However there are still issues with producing p-type ZnO, but the use of heterojunctions, where electrons from other p-type materials are injected into n-type ZnO material, could be a solution [13–15]. Also, the nanostructured morphologies in which ZnO can be grown greatly extend its technological potential and promise. Nanostructures in general are for example promising for sensing applications, because their surface area to volume ratio is much larger than that of bulk materials. For example, the adsorption and chemisorption of different gases onto ZnO alters the carrier density in the structures, and thus their electrical conductivity, making it possible to measure the different gas concentrations [16] and thus ZnO has been widely studied as a sensor [17,18]. It is also a biocompatible material, making it suitable for bio-sensing and other bio-applications [19,20].

ZnO nanostructures are also being studied as a field emitters or cold cathodes

[21,22]. Field emission, which is a quantum mechanical effect whereby free electrons, in a metal or a semiconductor, can tunnel into a vacuum in the presence of an applied electric field, but in the absence of heating. This has potential applications from flat panel displays and miniature x-ray sources to microelectronics and the nanostructured morphology possible for ZnO can lead to technological advantages in terms of increased field enhancement at the sharp nanostructure edges. This is essentially the field concentration effect familiar in macroscopic applications such as lightning rods.

The piezoelectric effect is the generation of an electric charge/voltage from the application of mechanical stress. The large degree of bond polarity together with the non-centro symmetric crystal structure of ZnO causes a pronounced piezoelectric effect [3] in this material which makes it suitable for electromechanical coupling applications like electrical nanogenerators [23–25] and surface acoustic wave (SAW) device technology [26]. Spintronics, or spin transport electronics, make use of the intrinsic spin and magnetic moment of an electron, in addition to its charge. There is some optimism, due to the reported observation of ferromagnetism in ZnO, of applications in this field also [27]. ZnO is also a transparent material making it a potential candidate for transparent electronics, such as solar cells [28,29].

#### **1.3** Thesis motivation

The primary area of interest for this work is the strong tendency of ZnO for selforganized growth of nanostructures with a large diversity of reported morphologies [30–36]. A selection of these morphologies is shown in Figure 1.4. This diversity, while being of interest for many applications, also suggests a growth morphology that is highly sensitive to the growth environment and thus intrinsically hard to control, especially if one is interested in large scale industrial applications.



Figure 1.4: Selection of TEM/SEM images of ZnO nanostructures taken from literature (a) nanowalls from Grabowska *et al.* [30], (b) nanoring from Wang *et al.* [36], (c)nanoflower from Sun *et al.* [34], (d) nanoneedles from Lorenz *et al.* [35], (e) nanowires grown in our system, (f) nanobelts from Wang *et al.* [36]

The majority of papers dealing with ZnO growth are experimental in nature, many detailing new morphologies, while the amount of theoretical work on the growth mechanism is rather limited. An example of the contributions to the theoretical underpinnings of the field is the work of Barnard *et al.*, who consider the formation of ZnO nanostructures theoretically, mainly based on thermodynamic issues and including the effects of surface energies, in addition to the effects of impurity incorporation [37, 38]. Also Subannajui *et al.*, using simulations, examine the optimum concentration of oxygen for ZnO nanowire growth in VPT systems [39]. While these provide interesting results, there is still a significant dearth of theoretical study and of models of the growth mechanisms/processes for ZnO nanostructures.

#### 1.4 Thesis outline

Without a comprehensive study of the theoretical basis of both the thermodynamic and kinetic aspects of the growth processes, and the associated fundamental scientific understanding of the processes, the ability to control and reproduce nanostructure growth, especially on large scales, will be hindered. One major advantage of a bottom-up approach, like the growth of ZnO nanostructure growth, is that it does not require expensive lithographic processing steps. However, the sensitivity of the nanostructure morphology based on bottom-up growth to a number of growth parameters may lead to significant variations in nanostructure length, diameter, positioning, spacing and morphology for similar growth conditions. In order for ZnO to be effective in the applications described above, reproducible ZnO nanostructure growth at industrial scales is required. This thesis aims to add to the current understanding of the ZnO nanostructure growth mechanism for VPT growth systems.

#### 1.4 Thesis outline

Chapter 1 has introduced the thesis and subject matter, motivation and background information on the material system. Chapter 2 begins with an overview of the growth methods available for ZnO nanowire growths; it describes the experimental work conducted in this thesis, which is divided into three stages: substrate preparation, VPT growth of ZnO nanowires and the characterisation of these nanowires.

Chapters 3 and 4 identify the processes by which ZnO nanostructures are formed in our growth system and we consider the possible condensing species involved in ZnO nanowire growth. Chapter 3 outlines the current status in the literature about the pathway to the formation of solid ZnO. We describe the thermodynamic analysis of Zn vapour, using currently available data on the Gibbs free energy of reactions, to calculate the partial pressure and saturation of the Zn vapour produced by the CTR of ZnO powder. After summarising the various literature reports on the molecular parameters of the gaseous ZnO molecule, we derive a model, using these parameters, to calculate the Gibbs free energy of the reaction to produce gaseous ZnO molecules. With this model we find the partial pressure and degree of saturation of the ZnO molecular vapour produced. Chapter 5 derives a model to calculate the energy barriers and rates of nucleation for both homogeneous and heterogeneous nucleation of ZnO vapour. The outcomes of Chapters 3, 4 and 5 is a conclusion on the involvement of both Zn vapour and ZnO molecular vapour in the growth process and offers a suggestion about one possible cause of the morphological diversity seen in the literature.

In Chapter 6 we discuss a model to calculate the growth rate and length of ZnO nanowires. The predicted dependence of the length of nanowires on the radius of the nanowire is compared to experimental measurements of the dimensions of ZnO nanowires grown via VPT. The observation of an inverse dependence of nanowire length on radius supports the inclusion of a diffusion term in the growth model. Chapter 7 provides a summary and discussion of the work of the work described in the previous chapters and proposes possible directions for future work, based on the conclusions from the thesis and unanswered questions still remaining.

### Bibliography

- A.K. Biswas. The primacy of india in brass and zinc metallurgy. Indian Journal of History of Science, 28(4):309–330, 1993.
- [2] William Kent. Scientific naming. *Philosophy of Science*, 25(3):185–193, 1958.
- [3] Andreas Waag Axel Hoffmann Jean Geurts Claus F. Klingshirn, Bruno K. Meyer. Zinc Oxide: From Fundamental Properties Towards Novel Applications. Springer, 2010.
- [4] C. Jagadish and S.J. Pearton. Zinc Oxide Bulk, Thin Films and Nanostructures:. Elsevier, 2006.
- [5] P Zu, ZK Tang, GKL Wong, M Kawasaki, A Ohtomo, H Koinuma, and Y Segawa. Ultraviolet spontaneous and stimulated emissions from ZnO microcrystallite thin films at room temperature. SOLID STATE COMMUNICA-TIONS, 103(8):459–463, AUG 1997.
- [6] DM Bagnall, YF Chen, MY Shen, Z Zhu, T Goto, and T Yao. Room temperature excitonic stimulated emission from zinc oxide epilayers grown by plasma-assisted MBE. JOURNAL OF CRYSTAL GROWTH, 184:605–609, FEB 1998.
  8th International Conference on II-VI Compounds, GRENOBLE, FRANCE, AUG 25-29, 1997.

- [7] DC Look. Recent advances in ZnO materials and devices. MATERIALS SCIENCE AND ENGINEERING B-SOLID STATE MATERIALS FOR AD-VANCED TECHNOLOGY, 80(1-3, SI):383–387, MAR 22 2001. 5th Bi-Annual Meeting of the International Workshop on Expert Evaluation and Control of Compound Semiconductor Materials and Technologies (EXMATEC 2000), HERALKION, GREECE, MAY 21-24, 2000.
- [8] Wurtzite crystal structure: http://en.wikipedia.org/wiki/wurtzite.
- [9] U Ozgur, YI Alivov, C Liu, A Teke, MA Reshchikov, S Dogan, V Avrutin, SJ Cho, and H Morkoc. A comprehensive review of ZnO materials and devices. *JOURNAL OF APPLIED PHYSICS*, 98(4), AUG 15 2005.
- [10] S Desgreniers. High-density phases of ZnO: Structural and compressive parameters. *PHYSICAL REVIEW B*, 58(21):14102–14105, DEC 1 1998.
- [11] A. Wander, F. Schedin, P. Steadman, A. Norris, R. McGrath, T. S. Turner, G. Thornton, and N. M. Harrison. Stability of polar oxide surfaces. *Phys. Rev. Lett.*, 86(17):3811–3814, Apr 2001.
- [12] B Meyer and D Marx. Density-functional study of the structure and stability of ZnO surfaces. *PHYSICAL REVIEW B*, 67(3), JAN 15 2003.
- [13] M. Willander, O. Nur, S. Zaman, A. Zainelabdin, N. Bano, and I. Hussain. Zinc oxide nanorods/polymer hybrid heterojunctions for white light emitting diodes. *JOURNAL OF PHYSICS D-APPLIED PHYSICS*, 44(22), JUN 8 2011. 12th International Symposium on the Science and Technology of Light Sources/3rd International Conference on White LEDs and Solid State Lighting, Eindhoven Univ, Eindhoven, NETHERLANDS, JUL 11-16, 2010.

- [14] Babak Nikoobakht, John Bonevich, and Andrew Herzing. 1D n-p Heterojunctions of Zinc Oxide on Gallium Nitride: A Structural Characterization. JOUR-NAL OF PHYSICAL CHEMISTRY C, 115(20):9961–9969, MAY 26 2011.
- [15] DC Look, B Claffin, YI Alivov, and SJ Park. The future of ZnO light emitters. *PHYSICA STATUS SOLIDI A-APPLIED RESEARCH*, 201(10):2203–2212, AUG 2004. Conference on Photo-Responsive Materials, Kariega Game Reserve, SOUTH AFRICA, FEB 25-29, 2004.
- [16] HT Wang, BS Kang, F Ren, LC Tien, PW Sadik, DP Norton, SJ Pearton, and J Lin. Hydrogen-selective sensing at room temperature with ZnO nanorods. *APPLIED PHYSICS LETTERS*, 86(24), JUN 13 2005.
- [17] Ang Wei, Liuhua Pan, and Wei Huang. Recent progress in the ZnO nanostructure-based sensors. MATERIALS SCIENCE AND ENGINEERING B-ADVANCED FUNCTIONAL SOLID-STATE MATERIALS, 176(18):1409– 1421, NOV 15 2011.
- [18] S. J. Pearton, F. Ren, Yu-Lin Wang, B. H. Chu, K. H. Chen, C. Y. Chang, Wantae Lim, Jenshan Lin, and D. P. Norton. Recent advances in wide bandgap semiconductor biological and gas sensors. *PROGRESS IN MATERIALS SCI-ENCE*, 55(1):1–59, JAN 2010.
- [19] Adam Dorfman, Nitin Kumar, and Jong-in Hahm. Nanoscale ZnO-enhanced fluorescence detection of protein interactions. ADVANCED MATERIALS, 18(20):2685+, OCT 17 2006.

- [20] Anish M. Kumar, Soyoun Jung, and Taeksoo Ji. Protein Biosensors Based on Polymer Nanowires, Carbon Nanotubes and Zinc Oxide Nanorods. SENSORS, 11(5):5087–5111, MAY 2011.
- [21] E. McCarthy, S. Garry, D. Byrne, E. McGlynn, and J. P. Mosnier. Field emission in ordered arrays of ZnO nanowires prepared by nanosphere lithography and extended Fowler-Nordheim analyses. *JOURNAL OF APPLIED PHYSICS*, 110(12), DEC 15 2011.
- [22] Xudong Wang, Jun Zhou, Changshi Lao, Jinhui Song, Ningsheng Xu, and Zhong L. Wang. In situ field emission of density-controlled ZnO nanowire arrays. ADVANCED MATERIALS, 19(12):1627+, JUN 18 2007.
- [23] Zhong Lin Wang. Towards Self-Powered Nanosystems: From Nanogenerators to Nanopiezotronics. ADVANCED FUNCTIONAL MATERIALS, 18(22):3553– 3567, NOV 24 2008.
- [24] Sheng Xu, Yong Qin, Chen Xu, Yaguang Wei, Rusen Yang, and Zhong Lin Wang. Self-powered nanowire devices. NATURE NANOTECHNOLOGY, 5(5):366–373, MAY 2010.
- [25] Mohammed Riaz, Jinhui Song, Omer Nur, Zhong Lin Wang, and Magnus Willander. Study of the Piezoelectric Power Generation of ZnO Nanowire Arrays Grown by Different Methods. ADVANCED FUNCTIONAL MATERIALS, 21(4):628–633, FEB 22 2011.
- [26] Wei-Shan Wang, Tsung-Tsong Wu, Tai-Hsu Chou, and Yung-Yu Chen. A ZnO nanorod-based SAW oscillator system for ultraviolet detection. NANOTECH-NOLOGY, 20(13), APR 1 2009.

- [27] SJ Pearton, WH Heo, M Ivill, DP Norton, and T Steiner. Dilute magnetic semiconducting oxides. SEMICONDUCTOR SCIENCE AND TECHNOLOGY, 19(10):R59–R74, OCT 2004.
- [28] Claus Klingshirn, J. Fallert, H. Zhou, J. Sartor, C. Thiele, F. Maier-Flaig,
   D. Schneider, and H. Kalt. 65 years of ZnO research old and very recent results. *PHYSICA STATUS SOLIDI B-BASIC SOLID STATE PHYSICS*, 247(6):1424–1447, JUN 2010.
- [29] Claes G. Granqvist. Transparent conductors as solar energy materials: A panoramic review. SOLAR ENERGY MATERIALS AND SOLAR CELLS, 91(17):1529–1598, OCT 15 2007.
- [30] J Grabowska, A Meaney, KK Nanda, JP Mosnier, MO Henry, JR Duclere, and E McGlynn. Surface excitonic emission and quenching effects in ZnO nanowire/nanowall systems: Limiting effects on device potential. *PHYSICAL REVIEW B*, 71(11), MAR 2005.
- [31] Jie Wang, Huizhao Zhuang, Junlin Li, and Peng Xu. Synthesis, morphology and growth mechanism of brush-like ZnO nanostructures. APPLIED SURFACE SCIENCE, 257(6):2097–2101, JAN 1 2011.
- [32] Chatchawal Wongchoosuk, Kittitat Subannajui, Andreas Menzel, Iris Amarilio Burshtein, Shoshana Tamir, Yeshayahu Lifshitz, and Margit Zacharias. Controlled Synthesis of ZnO Nanostructures: The Role of Source and Substrate Temperatures. JOURNAL OF PHYSICAL CHEMISTRY C, 115(3):757–761, JAN 27 2011.
- [33] R. T. Rajendra Kumar, E. McGlynn, M. Biswas, R. Saunders, G. Trolliard, B. Soulestin, J. R. Duclere, J. P. Mosnier, and M. O. Henry. Growth of ZnO nanostructures on Au-coated Si: Influence of growth temperature on growth mechanism and morphology. *JOURNAL OF APPLIED PHYSICS*, 104(8), OCT 15 2008.
- [34] XH Sun, S Lam, TK Sham, F Heigl, A Jurgensen, and NB Wong. Synthesis and synchrotron light-induced luminescence of ZnO nanostructures: Nanowires, nanoneedles, nanoflowers, and tubular whiskers. JOURNAL OF PHYSICAL CHEMISTRY B, 109(8):3120–3125, MAR 3 2005.
- [35] M Lorenz, EM Kaidashev, A Rahm, T Nobis, J Lenzner, G Wagner, D Spemann, H Hochmuth, and M Grundmann. MgxZn1-xO (0 i= x i 0.2) nanowire arrays on sapphire grown by high-pressure pulsed-laser deposition. APPLIED PHYSICS LETTERS, 86(14), APR 4 2005.
- [36] ZL Wang. Zinc oxide nanostructures: growth, properties and applications. JOURNAL OF PHYSICS-CONDENSED MATTER, 16(25):R829–R858, JUN 30 2004.
- [37] Hong Jin Fan, Amanda S. Barnard, and Margit Zacharias. ZnO nanowires and nanobelts: Shape selection and thermodynamic modeling. APPLIED PHYSICS LETTERS, 90(14), APR 2 2007.
- [38] AS Barnard, Y Xiao, and Z Cai. Modelling the shape and orientation of ZnO nanobelts. CHEMICAL PHYSICS LETTERS, 419(4-6):313–316, FEB 26 2006.
- [39] Kittitat Subannajui, Niranjan Ramgir, Raphael Grimm, Rebecca Michiels, Yang Yang, Stefan Mueller, and Margit Zacharias. ZnO Nanowire Growth:

A Deeper Understanding Based on Simulations and Controlled Oxygen Experiments. *CRYSTAL GROWTH & DESIGN*, 10(4):1585–1589, APR 2010.

# Chapter 2

# Experimental methods

# 2.1 Introduction

This chapter describes the methods used to conduct the experimental work reported in this thesis. A brief overview of the methods available for the growth of ZnO nanowires is given. The study of ZnO nanowire growth in this thesis is divided into three stages:

- 1: Preparing the growth substrate with a ZnO buffer layer.
- 2: Growing ZnO nanowires in a VPT system.
- 3: Characterising the ZnO nanowires produced.

This chapter discusses each stage, detailing the methods and equipment used.

## 2.2 Overview of methods for growing ZnO nanowires

There are various methods for growing ZnO nanowires. All of these methods involve production and transport of the source species to the substrate, followed by impingement and incorporation of that material into a nanowire. Growth methods generally differ in both how the source species are generated and how they are transported to the substrate.

This thesis discusses ZnO nanowires grown via a VPT method. VPT is one of the most popular techniques for growing ZnO nanowires. This method was used to grow the first ZnO nanowires produced during the recent period of interest in ZnO research [1]. Section 2.4 describes this method in more detail.

In chemical vapour deposition (CVD) methods the source species is transported to the substrate in vapour form via a carrier gas. One type of CVD is metal organic vapour phase epitaxy (MOVPE), also known as metal-organic chemical vapour deposition (MOCVD) when the material is grown via deposition rather than epitaxy, is a chemical vapour-based method of epitaxial growth of materials based on the surface reaction of organic compounds, or metal-organics and metal hydrides, containing the required chemical elements. The vapour of the source material is transported to the substrate, via a carrier gas, where the growth of crystals takes place by chemical reaction rather than physical deposition. This deposition does take place in a vacuum, but in the gas phase at moderate pressures (2 to 100 kPa). MOVPE is more commonly used to grow III-V semiconductor nanowires [2,3] than ZnO nanowires, however, ZnO nanostructures have been grown using diethylzinc (DEZn) and nitrous oxide  $(N_2O)$  as source materials [4,5]. One strength MOVPE has is the ability to control the exact gas composition in the growth chamber. Growth takes place at relatively low temperatures of  $\sim 700$  K, but the equipment required for a MOVPE set-up is complicated and costly.

Physical vapour deposition (PVD) methods, including molecular beam epitaxy (MBE), pulsed laser deposition (PLD) and sputtering methods, are popular for

growing thin films of ZnO, but can also be used to grow ZnO nanostructures. MBE is a common thin film deposition technique, involving the reaction of one or more thermal beams of atoms or molecules with a substrate in ultrahigh vacuum  $(1 \times 10^{-8}$ Pa). Gas phase MBE can also be used to grow ZnO nanorods [6]. In the PLD technique, a high-power pulsed laser beam in a vacuum chamber is focused on a target of the material to be deposited. This target material is vapourized (in a plasma plume) and is then deposited as a thin film or nanostructured growth on a substrate. PLD can take place in ultra-high vacuum or in the presence of a background gas, such as oxygen, which is commonly used when depositing oxides, to fully oxygenate the deposited films. For ZnO deposition either a ZnO pressedpowder target or a Zn metal target is used as a source. PLD can be used to grow ZnO nanostructures directly [7–9], or to deposit a ZnO film for use as a template for subsequent ZnO nanostructure growth by other growth methods (such as VPT [10]). This method produces high quality ZnO nanowires, however the required equipment and operating costs are expensive.

An increasingly popular method for growing ZnO nanowires is chemical bath deposition (CBD) [11–13], where the production of the source species and its transport to the substrate takes place in solution. CBD is based on the formation of a solid phase from a solution. In the CBD procedure, the substrate is immersed in an aqueous solution containing the precursors. Zn salts such as zinc acetate, nitrate, sulphate and chloride are used with a base, to form soluble zinc hydroxide. Zinc hydroxide decomposes to form ZnO. Many different bases can be used in this method, such a hexamine (HMT), ammonia, urea, and sodium hydroxide. Different combinations of the base, zinc salt, substrate and choice of solvent, can influence the final morphology of the resulting ZnO nanostructures. This synthesis can be carried out at a relatively low temperature ( $< 100^{\circ}$  C), making it suitable for substrates, such as plastics, that cannot be heated to the high temperatures required in other systems. The equipment required is simple, often just a hotplate and beaker, making this a relatively cheap growth method. The sample quality, especially the optical quality, of the ZnO nanowires produced are not generally as good as those grown in methods using high temperatures. CBD can also be used in combination with other growth methods to produce ZnO nanowires [14]. For example, we use a CBD process to deposit ZnO buffer layers on our substrates, in preparation for subsequent VPT growth of ZnO nanowires.

# 2.3 Growth substrate and preparation for ZnO nanowire growth

This section outlines the choice and methods for preparing substrates for ZnO nanowire growth via VPT.

## 2.3.1 Substrate choice and cleaning

This work used silicon wafer substrates with either (100) or (111) orientation. We chose silicon as it is compatible for visualisation with the SEM and is relatively inexpensive. Sapphire ( $Al_2O_3$ ) can also be used for VPT growth of aligned ZnO nanowires [15–17]. However, in addition to being more costly, sapphire is electrically insulating, making it unsuitable for standard SEM studies.

A silicon wafer was cleaved to form  $2.0 \text{ cm} \times 1.0 \text{ cm}$  substrates. These substrates were sonicated in acetone for 10 minutes, rinsed in ethanol and dried under a stream of nitrogen. We made no attempt to remove the native oxide layer and no differences in subsequent results for growth on Si with either the (100) or (111) orientation was observed.

## 2.3.2 Seed layer choice

Experiments indicate that ZnO nanowire growth does not take place on bare  $Si/SiO_2$  substrates (i.e. those without seeds of some type, either ZnO or metal catalysts). Seeds are deposited on the substrate to provide energetically suitable accommodation sites for ad-atoms, which enable nucleation and nanowire growth.

Two growth modes are normally observed in seed-assisted nanowire growth; vapour liquid solid (VLS) and vapour solid (VS). The VLS growth mode operates with metal seed particles and was first proposed by Wagner and Ellis, in 1964, to describe growth of silicon whiskers using gold seeds [18]. In VLS growth, the seed particle and growth precursor (in this case Zn) form a liquid alloy resulting in nanowire growth by precipitation from a supersaturated solution [3] and subsequent Zn oxidation. In VS growth, the seed particle provides an energetically favourable nucleation/accommodation site for preferential deposition. Nanowires grown via VLS have seed particles visible on top of the wire (as illustrated in Figure 2.1), unlike those grown via VS.



Figure 2.1: Illustration of the VLS growth mode

Au has been widely used in metal seed-assisted growth of ZnO nanowries. Nano wires grown using Au seeds on a silicon substrate have shown both VLS and VS growth modes, producing nanowires both with and without Au caps [19,20]. Growth systems, using lower temperatures typically only observe VLS growth. At high temperatures, Au present can migrate, or bead, making it incompatible with a VLS growth mode. Our system uses a comparatively high growth temperature, making the use of Au (which is successful in other systems) unsuitable for our work as the growth mode is unpredictable (i.e. can be either VS or VLS) making modelling difficult. ZnO nanowires grown on a Au film, on a Si/SiO<sub>2</sub> substrate, do not generally align normal to the substrate [16,19,21]. Figure 2.2 shows the result of VPT growth of ZnO nanowires on a substrate with a deposited gold film. The gold film was deposited using a standard bell jar thermal evaporator.



Figure 2.2: ZnO nanowires grown on deposited gold seeds

A buffer layer of ZnO on a  $Si/SiO_2$  substrate can also provide energetically suitable nucleation sites for ZnO nanowire growth. VPT growth on a buffer layer of ZnO results in well-aligned ZnO nanowire growth in a VPT growth system, as shown in Figure 2.3. ZnO nanowires grown on *c*-axis textured ZnO buffer layers will grow via a VS growth mode. Greene [22] originally developed a versatile method for producing a textured buffer layer deposition and Dr. Daragh Byrne, in our group studied and further developed the method [23]. 2.3 Growth substrate and preparation for ZnO nanowire growth



Figure 2.3: ZnO nanowires grown on a ZnO buffer layer

## 2.3.3 Buffer layer deposition

The buffer layer is prepared in two stages. In the first stage, a layer of textured/aligned seeds of ZnO are deposited. This is followed, in the second stage by a short CBD stage to provide nucleation sites for subsequent VPT growth as illustrated in Figure 2.4.

#### Drop coating

In the first stage of the buffer-layer deposition, ZnO seeds are deposited by a drop coating method. A solution of 5.0 mM zinc acetate is prepared by dissolving zinc acetate dihydrate (Sigma Aldrich, 99%) in reagent grade ethanol (Sigma Aldrich, 99.8%). The solution is sonicated until the zinc acetate is fully dissolved. This reaction is extremely sensitive to water vapour, so it is necessary to use fresh ethanol that is uncontaminated with water from the atmosphere. A drop of this solution is placed on the silicon substrate (Wacker Chemitronic GMBH) using a pipette. The volume of the droplet required was calculated, by measuring the sample size, so that there is a coverage of ~  $3.75 \ \mu l/cm^2$ . The droplet is allowed to remain on the surface for 20 s. The sample is rinsed with fresh ethanol and gently dried under a stream of nitrogen. This process is repeated four times, or more, if the relative humidity in the laboratory is low. The sample is then annealed at 350 °C, for 30 minutes, in a furnace, resulting in a thin layer of ZnO seeds on the Si/SiO<sub>2</sub> substrate between 2-4 nm height and 10-20 nm in diameter, providing nucleation sites for the following CBD growth step. The full details of and mechanism behind this drop coating process, developed by Dr Daragh Byrne, is given in reference [23].



Figure 2.4: Two stages of buffer layer deposition (a) ZnO seed layer (b) Chemical bath deposition ZnO layer

#### Chemical bath deposition

The CBD layer is formed by the thermal decomposition of zinc acetate, in solution, to form zinc oxide. Zinc acetate (Sigma Aldrich, 99%) is dissolved in de-ionized water to form a 25.0 mM solution. The Si/SiO<sub>2</sub> substrates, prepared with deposited ZnO seeds from the drop coating stage, are suspended in 125 ml of this solution, using a wire holder. This solution is heated a hotplate, with slow stirring until the solution reaches 65 °C. After 80 minutes this solution is discarded. The sample is now placed in a fresh solution of 25 mM zinc acetate. Care must be taken to prevent clumps of precipitate building up on the surface, by gently moving sample, to remove bubbles gathering on the suspended substrate surface. The solution is again slowly heated to 65 °C and maintained at this temperature for a further 80 minutes. After deposition the substrate is removed and rinsed with deionized water. This stage deposits a layer of CBD nanorods between 150-300 nm in length.

Both stages of the buffer layer deposition process can be scaled up, so that an entire wafer of silicon can be prepared with a ZnO buffer layer at one time. This wafer is then cleaved into samples of  $2.0 \text{ cm} \times 1.0 \text{ cm}$ , with little or no damage to the deposited ZnO buffer layer.

#### Removing the double buffer layer

To provide an unseeded area of a sample, for comparison purposes, the buffer layer is removed from a portion of a sample. A small area of the sample is dipped in  $H_2SO_4$  for 5-10 s. The sample is rinsed repeatedly with de-ionized water and dried under a stream of nitrogen. This provides a sample for VPT growth with both bare Si/SiO<sub>2</sub> substrate and ZnO buffer layer deposited areas.

#### 2.4 Vapour phase transport growth of ZnO nanowires

VPT is among the most straightforward methods available for high quality ZnO nanowire growth [24–26]. The main equipment required for VPT is a furnace. The growth generally takes place at or close to atmospheric pressure, making this a relatively cost-effective process. Source material is produced at high temperatures in a furnace, and transported in vapour form to the substrate, where it is deposited. Traditionally, the substrate is placed downstream from the source species [16], however, in this work the substrate is placed directly above the source powders, giving a more uniform growth distribution and well as providing a somewhat enclosed space in the sample-source powder region in the chamber in which our equilibrium thermodynamic analysis is likely to better describe the growth environment.

CTR is used to produce Zn vapour from ZnO source powder for ZnO nanowire growth in VPT systems. Carbon acts as a reducing agent on ZnO powder, allowing Zn vapour to be generated at lower temperatures than the direct sublimation of ZnO. The reducing reactions are described by the following equations:

$$T < 973 \text{ K} \quad \text{ZnO}(s) + \frac{1}{2}\text{C}(s) \rightarrow \text{Zn}(g) + \frac{1}{2}\text{CO}_2(g)$$

$$T > 973 \text{ K} \quad \text{ZnO}(s) + \text{C}(s) \rightarrow \text{Zn}(g) + \text{CO}(g)$$

$$(2.1)$$

Significant sublimation of ZnO takes place only at temperatures > 2250 K and thus CTR allows Zn vapour to be produced from ZnO source powders at much lower temperatures of ~ 1200 K, which are easier to achieve. Zn vapour can also be produced at relatively low temperatures of 700-800 K, by direct evaporation of Zn metal [27–29]. However, in our experiments this process yielded unpredictable results, with uncontrolled ZnO deposition throughout the entire hot zone in the furnace and inconsistent ZnO nanowire morphology.

The double buffer seed layer provides nucleation sites for ZnO nanowire growth, by VPT, as illustrated in Figure 2.5.



Figure 2.5: Illustration of ZnO nanowires grown by CTR-VPT on substrates prepared with a deposited ZnO buffer layer

## 2.4.1 Growth procedure for VPT

The experimental set up for VPT growth is depicted in Figure 2.6. Equal amounts (usually 0.060 g) of ZnO powder (Alfa Aesar, 99.9995%) and graphite (Alfa Aesar, 99.9999%) are mixed together in a pestle and mortar. The resulting mixture is placed in an alumina boat and spread evenly over a width of 1.5 cm and length 1.0 cm. Two rectangles of silicon are placed on the top edge of the alumina boat. The prepared substrate (a buffer layer of ZnO on a Si/SiO<sub>2</sub> substrate) is placed face down on the silicon supports directly above the powder. The sample is ~ 1.0 cm above the powders.

This boat is then placed in the centre of a quartz tube (length: 115cm, internal diameter: 37mm), positioned in a Lenton Thermal Designs single temperature zone

horizontal tube furnace. One end of the furnace is attached to gas lines for argon and oxygen via Mass Flow Controllers (Analyt GFC17). The other end is connected to an exhaust line. The pressure in the furnace is 1 atm, as the furnace is open to the external atmosphere, via the exhaust.

An argon flow of 90 sccm is used to flush the furnace for 10-15 minutes. This flow of argon is continued for the duration of the growth. The furnace is heated to between 1173-1273 K, which takes approximately 10 minutes and is kept at this temperature for one hour. The furnace is then allowed to cool for several hours before the argon is turned off and the sample removed.



Figure 2.6: Illustration of experimental set up for VPT growth

#### 2.4.2 Furnace temperature

The temperature of the furnace is assumed to reach the growth temperature and remain constant for the duration of the growth. Figure 2.7 below shows that the measured temperature of the furnace overshoots the set temperature by more than 100 K before settling to a value  $\sim 50$  K higher than the set temperature.



Figure 2.7: Furnace temperature as a function of time

# 2.4.3 Growth duration

A growth time of one hour is standard for ZnO nanowire VPT growth. We conducted a series of timed experiments to determine the exact amount of time during which nanowire growth takes place.

We examined three samples grown over different times. Samples were placed in the furnace for growth times of 45, 30 and 15 minutes. No difference in nanowire length or density is observed in samples with growth times of 45 and 30 minutes, however, the nanowires on the sample with a growth time of 15 minutes showed shorter nanowires. We can say that the growth time is greater than 15 minutes and is less than 30 minutes. For the calculations in Chapter 6 we use a growth time of 30 minutes for samples grown in this way, regardless of how long the sample is in the furnace as these results suggest that the growth has stopped for times greater than 30 minutes.

For various reasons growth does not take place for the entire experimental duration. When the sample is removed from the furnace a crust of ZnO powder is observed on the remaining mixed powders, suggesting that the reaction is quenched before the entire available powder mix is consumed due to re-deposition of ZnO on the powder surface with no carbon in the vicinity and hence the formation of an impermeable skin for longer growth periods. When the furnace is flushed with argon, it reduces the amount of Zn vapour and residual O<sub>2</sub> present. The growth makes use of the residual O<sub>2</sub> present in the furnace after a flushing period of 10-15minutes. The volume of the furnace tube is  $1237 \text{ cm}^3$ . The flow of argon of 90 sccm, flushes the furnace in less than 30 minutes. This depletes the amount of residual O<sub>2</sub> present in the furnace, retarding the growth. Both of these effects combine to yield an effective upper limit on the growth time of 30 minutes.

#### 2.4.4 Oxygen introduction

For the purpose of theoretical analysis we need to know the amount of  $O_2$  present in the furnace. The method described in Section 2.4.1 utilizes residual  $O_2$  present in the furnace after the short flushing period. The furnace, when flushed for 10-15 minutes prior to growth, contains the  $O_2$  required for ZnO nanowire growth. To ensure that the amount of  $O_2$  present is known, all of the residual  $O_2$  must be purged from the furnace, and an exact amount of  $O_2$  introduced. To remove the residual  $O_2$ , the furnace is flushed for 50 minutes with Ar before increasing the temperature. When a VPT growth is attempted after this purge is performed no ZnO nanowire growth is observed, indicating that all of the residual  $O_2$  has successfully been removed. After this 50 minute flushing period, a small amount (< 5.0 sccm) of  $O_2$  is introduced. The amount of  $O_2$  must be relatively small as the reaction between graphite and  $O_2$  is energetically favourable. When there is too much  $O_2$  present, the graphite will be used up in the reaction  $C + O_2 \rightarrow CO_2$  rather than being available for the CTR of ZnO powder. Performing growths at varying  $O_2$  amounts and observing the resulting growth, allowed us to determine the optimal value of 2.0 sccm for use.

The mass flow controller (MFC) used to control the amount of  $O_2$  introduced is designed for use at larger flow rates, such as the value of 90 sccm for the Ar flow. To determine the exact rates of  $O_2$  introduced to the furnace, the output volume of the MFC was measured for a certain time (as illustrated in Figure 2.8). The measured values were found not to match the value displayed on the MFC for small volumes. The measured values were used to calculate the partial pressure of the  $O_2$  present in the furnace.

#### 2.5 Characterisation



Figure 2.8: Illustration of apparatus to measure the actual  $O_2$  gas flow from MFC

Displayed value (sccm)	Measured value (sccm)
5.0	1.0
6.0	2.0
7.0	4.0
8.0	6.0
13.0	10.0

Table 2.1: Comparison between measured gas flow value and value displayed on MFC

#### 2.5 Characterisation

This section discusses the characterisation of the ZnO nanowires grown via VPT. There are many techniques currently in use to characterise ZnO nanowires, they can be divided into two main areas; techniques to examine the material properties of the nanowires and techniques to observe their surface morphology.

Material property characterization techniques include X-ray diffraction (XRD),

X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL). XRD can be used to examine the crystal structure of a material giving information about the composition of the material, the material texture and the epitaxial relationship of the material relative to the substrate. XPS makes use of the photoelectric effect to determine the elemental composition and chemical state of a material. PL uses the absorption and re-emission of light to measure the difference in energy between electronic energy levels. A PL spectrum provides information on the electronic structure of the material examined and can identify defects present. In this thesis we rely mainly on previous work characterising the material properties of the ZnO nanowires grown using our system [14, 23] to confirm the quality of the crystal structure.

The primary characterisation concern in this thesis is to observe the morphology and to measure the dimensions of the nanowires. Optical microscopy generally has a resolution limit of  $\sim 200$  nm making it unsuitable for observing nanowires with radii of the order, and often less than, this resolution limit. Scanning probe microscopy systems such as an atomic force microscopy (AFM) have extremely high-resolutions on the order of nanometers. AFM instruments measure the force of interaction between a small tip mounted on a cantilever and the surface of the sample. However, AFM imaging is more suitable for observation of objects with a lower aspect ratio than the nanowires we produce, such as the drop coated seed layer described in Section 2.3.3 [23]. It also has a relatively slow scan speed, making AFM unsuitable for providing an overview of an entire sample. A Scanning Electron Microscope (SEM) demonstrates a resolution capability of  $\sim 1-20$  nm with almost real-time scanning speeds making it perfect for the visualisation of individual ZnO nanowires and to provide an overview of the density of growth over a sample.

### 2.5.1 Scanning electron microscope imaging

A scanning electron microscope (SEM) is a type of electron microscope that uses an electron beam to form an image of an object. The beams of electrons are controlled using electromagnetic lenses. The electrons are generated in a filament (in our system) and accelerated by the anode. The electron beam is then focussed, by magnetic coils/magnetic lenses capable of bending the electron beam, as is illustrated schematically in Figure 2.9. In the scanning electron microscope, the electron beam is focussed to a fine point and swept across the specimen in a raster scanning procedure.

This electron beam interacts with the sample atoms in various ways, such as elastic or inelastic scattering, resulting in different emissions. These emissions are detected and analysed to give point by point information about the surface which is then built up to form the sample image. Secondary electrons are ejected from the surface atoms by inelastic scattering with the beam electrons and these are the main emission type by which morphological and topological information is obtained from a SEM. These emitted electrons are detected and analysed to give an image of the surface. The resolution of the SEM is dependent on the beam spot size, which depends on the wavelength of the electron beam. The samples need to be conductive to be imaged in the SEM because of the incident electron beam and the consequent charging effects for non-conductive samples. The SEM used to image samples in this thesis is a EVOLS15 from Karl-Zeiss, the gun uses a Lab6 filament and the resolution is 2 nm.



Figure 2.9: Schematic of SEM adapted from [30]

# 2.5.2 Image analysis

To measure the dimensions of the nanowires, images are taken in the SEM at an angle at or close to 90°, the lengths and radii of the ZnO nanowires are measured from these cross-sectional SEM images. The images from the SEM are analyzed using ImageJ [31]. ImageJ is a freely available software, written in Java for image processing and analysis.

# Bibliography

- PD Yang, HQ Yan, S Mao, R Russo, J Johnson, R Saykally, N Morris, J Pham, RR He, and HJ Choi. Controlled growth of ZnO nanowires and their optical properties. ADVANCED FUNCTIONAL MATERIALS, 12(5):323–331, MAY 2002.
- [2] Jessica Bolinsson, Philippe Caroff, Bernhard Mandl, and Kimberly A. Dick. Wurtzite-zincblende superlattices in InAs nanowires using a supply interruption method. NANOTECHNOLOGY, 22(26), JUL 1 2011.
- [3] Kimberly A. Dick, Philippe Caroff, Jessica Bolinsson, Maria E. Messing, Jonas Johansson, Knut Deppert, L. Reine Wallenberg, and Lars Samuelson. Control of III-V nanowire crystal structure by growth parameter tuning. SEMICON-DUCTOR SCIENCE AND TECHNOLOGY, 25(2, SI), FEB 2010.
- [4] C. Thiandoume, J. Barjon, O. Ka, A. Lusson, P. Galtier, and V. Sallet. Morphology transition of one-dimensional ZnO grown by metal organic vapour phase epitaxy on (0001)-ZnO substrate. *JOURNAL OF CRYSTAL GROWTH*, 311(18):4311–4316, SEP 1 2009.
- [5] K Ogata, K Maejima, S Fujita, and S Fujita. Growth mode control of ZnO toward nanorod structures or high-quality layered structures by metal-organic

vapor phase epitaxy. *JOURNAL OF CRYSTAL GROWTH*, 248:25–30, FEB 2003. 11th International Conference on Metalorganic Vapor Phase Epitaxy, BERLIN, GERMANY, JUN 03-07, 2002.

- [6] L. C. Tien, D. P. Norton, S. J. Pearton, Hung-Ta Wang, and F. Ren. Nucleation control for ZnO nanorods grown by catalyst-driven molecular beam epitaxy. *APPLIED SURFACE SCIENCE*, 253(10):4620–4625, MAR 15 2007.
- [7] D. Valerini, A. P. Caricato, M. Lomascolo, F. Romano, A. Taurino, T. Tunno, and M. Martino. Zinc oxide nanostructures grown by pulsed laser deposition. *APPLIED PHYSICS A-MATERIALS SCIENCE & PROCESSING*, 93(3):729– 733, NOV 2008.
- [8] T. Premkumar, P. Manoravi, K. Panigrahi, and K. Baskar. Particulate assisted growth of ZnO nanorods and microrods by pulsed laser deposition. APPLIED SURFACE SCIENCE, 255(15):6819–6822, MAY 15 2009.
- [9] R O'Haire, A Meaney, EG McGlynn, MO Henry, JR Duclere, and JP Mosnier. Growth of crystalline ZnO nanostructures using pulsed laser deposition. *SU-PERLATTICES AND MICROSTRUCTURES*, 39(1-4):153–161, JAN-APR 2006. Symposium on ZnO and Related Materials held at the 2005 Spring Meeting of the European-Materials-Research-Society, Strasbourg, FRANCE, MAY 31-JUN 03, 2005.
- [10] S. Garry, E. McCarthy, J. P. Mosnier, and E. McGlynn. Control of ZnO nanowire arrays by nanosphere lithography (NSL) on laser-produced ZnO substrates. APPLIED SURFACE SCIENCE, 257(12):5159–5162, APR 1 2011.

#### BIBLIOGRAPHY

- [11] Qingwei Li, Jiming Bian, Jingchang Sun, Jingwei Wang, Yingmin Luo, Kaitong Sun, and Dongqi Yu. Controllable growth of well-aligned ZnO nanorod arrays by low-temperature wet chemical bath deposition method. APPLIED SUR-FACE SCIENCE, 256(6):1698–1702, JAN 1 2010.
- [12] L. L. Yang, Q. X. Zhao, M. Willander, and J. H. Yang. Effective way to control the size of well-aligned ZnO nanorod arrays with two-step chemical bath deposition. *JOURNAL OF CRYSTAL GROWTH*, 311(4):1046–1050, FEB 1 2009.
- [13] Lori E. Greene, Benjamin D. Yuhas, Matt Law, David Zitoun, and Peidong Yang. Solution-grown zinc oxide nanowires. *INORGANIC CHEMISTRY*, 45(19):7535–7543, SEP 18 2006.
- [14] D. Byrne, E. McGlynn, M. O. Henry, K. Kumar, and G. Hughes. A novel, substrate independent three-step process for the growth of uniform ZnO nanorod arrays. *THIN SOLID FILMS*, 518(16, Sp. Iss. SI):4489–4492, JUN 1 2010.
- [15] M. Biswas, E. McGlynn, and M. O. Henry. Carbothermal reduction growth of ZnO nanostructures on sapphire-comparisons between graphite and activated charcoal powders. *MICROELECTRONICS JOURNAL*, 40(2, Sp. Iss. SI):259– 261, FEB 2009.
- [16] J Grabowska, KK Nanda, E McGlynn, JP Mosnier, and MO Henry. Studying the growth conditions, the alignment and structure of ZnO nanorods. SUR-FACE & COATINGS TECHNOLOGY, 200(1-4):1093–1096, OCT 1 2005.
- [17] J Grabowska, KK Nanda, E McGlynn, JP Mosnier, MO Henry, A Beaucamp, and A Meaney. Synthesis and photoluminescence of ZnO nanowires/nanorods.

JOURNAL OF MATERIALS SCIENCE-MATERIALS IN ELECTRONICS, 16(7):397–401, JUL 2005.

- [18] RS WAGNER and WC ELLIS. VAPOR-LIQUID-SOLID MECHANISM OF SINGLE CRYSTAL GROWTH ( NEW METHOD GROWTH CATALYSIS FROM IMPURITY WHISKER EPITAXIAL + LARGE CRYSTALS SI E ). APPLIED PHYSICS LETTERS, 4(5):89–&, 1964.
- [19] R. T. Rajendra Kumar, E. McGlynn, M. Biswas, R. Saunders, G. Trolliard, B. Soulestin, J. R. Duclere, J. P. Mosnier, and M. O. Henry. Growth of ZnO nanostructures on Au-coated Si: Influence of growth temperature on growth mechanism and morphology. *JOURNAL OF APPLIED PHYSICS*, 104(8), OCT 15 2008.
- [20] Dong Sik Kim, Roland Scholz, Ulrich Goesele, and Margit Zacharias. Gold at the root or at the Tip of ZnO Nanowires: A Model. SMALL, 4(10):1615–1619, OCT 2008.
- [21] R. T. Rajendra Kumar, J. Grabowska, J. P. Mosnier, M. O. Henry, and E. McGlynn. Morphological control of ZnO nanostructures on silicon substrates. *SUPERLATTICES AND MICROSTRUCTURES*, 42(1-6):337–342, JUL-DEC 2007.
- [22] LE Greene, M Law, DH Tan, M Montano, J Goldberger, G Somorjai, and PD Yang. General route to vertical ZnO nanowire arrays using textured ZnO seeds. NANO LETTERS, 5(7):1231–1236, JUL 2005.
- [23] D. Byrne, E. McGlynn, K. Kumar, M. Biswas, M. O. Henry, and G. Hughes. A Study of Drop-Coated and Chemical Bath-Deposited Buffer Layers for Va-

por Phase Deposition of Large Area, Aligned, Zinc Oxide Nanorod Arrays. CRYSTAL GROWTH & DESIGN, 10(5):2400–2408, MAY 2010.

- [24] CH Ye, XS Fang, YF Hao, XM Teng, and LD Zhang. Zinc oxide nanostructures: Morphology derivation and evolution. JOURNAL OF PHYSICAL CHEM-ISTRY B, 109(42):19758–19765, OCT 27 2005.
- [25] Kittitat Subannajui, Niranjan Ramgir, Raphael Grimm, Rebecca Michiels, Yang Yang, Stefan Mueller, and Margit Zacharias. ZnO Nanowire Growth: A Deeper Understanding Based on Simulations and Controlled Oxygen Experiments. CRYSTAL GROWTH & DESIGN, 10(4):1585–1589, APR 2010.
- [26] D. S. Kim, U. Goesele, and M. Zacharias. Surface-diffusion induced growth of ZnO nanowires. JOURNAL OF CRYSTAL GROWTH, 311(11):3216–3219, MAY 15 2009.
- [27] Zengxing Zhang, Yuanchun Zhao, Lianfeng Sun, Dongfang Liu, Jun Shen, Weiya Zhou, Qiang Luo, Aizi Jin, Haifang Yang, Changzhi Gu, and Sishen Xie. Growth and Electrical Properties of Zinc Oxide Nanowires. *JOURNAL OF NANOSCIENCE AND NANOTECHNOLOGY*, 9(2):1119–1122, FEB 2009. 6th International Conference on Nanoscience and Technology, Beijing, PEO-PLES R CHINA, JUN 04-06, 2007.
- [28] Seungjun Oh, Mina Jung, Jieun Koo, Youngji Cho, Sungkuk Choi, Samnyung Yi, Gyungsuk Kil, and Jiho Chang. The mechanism of ZnO nanorod growth by vapor phase transportation. *PHYSICA E-LOW-DIMENSIONAL SYSTEMS* & NANOSTRUCTURES, 42(9):2285–2288, JUL 2010.

#### BIBLIOGRAPHY

- [29] Tae-Woong Koo and Dongmok Whang. GROWTH OF HIGH QUALITY ZINC OXIDE NANOWIRES BY SIMPLE OXIDATION OF ZINC POWDER IN AIR. NANO, 3(6):477–482, DEC 2008.
- [30] R.A. Freedman H.D Young. University Physics. Addison-Wesley, 1996.
- [31] http://rsbweb.nih.gov/ij/.

# Chapter 3

# Thermodynamic analysis of Zn vapour

# 3.1 Introduction

As discussed in Chapter 2, one of the most widely used methods to grow ZnO nanostructures is VPT with Zn vapour generated by the CTR of ZnO powder. Nanowire growth, via VPT, involves four main stages, as shown by the schematic representation in Figure 3.1:

I: Generation of source species

- II: Transport of source species to the substrate
- III: Impingement of material on to the substrate i.e. condensation
- IV: Diffusion on the substrate and incorporation of material into a nanostrucure

This chapter will focus on the production of the source species and the impingement of the material onto the substrate for ZnO nanowire growth.

In this thesis we identify the process by which solid ZnO is formed in our growth system and in doing so, determine the possible condensing species involved in ZnO nanowire growth. Various authors have suggested that ZnO growth proceeds via different paths. Kubo *et al.* [1] assume that ZnO molecular vapour condenses to form

#### 3.1 Introduction



Figure 3.1: Illustration of the stages of VPT growth of nanostructures

solid ZnO in their molecular dynamics simulation of ZnO homoepitaxial growth. In a model to describe ZnO nanowire growth with gold seed particles, Kim *et al.* [2] also suggest that ZnO gaseous molecules condense to form solid ZnO. However, Hejazi and Hosseini [3] in their model of gold catalyzed growth assume that the condensing species is Zn vapour, which is subsequently oxidized to form solid ZnO. In a simulation of ZnO nanowire growth examining the effect of gas flow on the growth system, Subannajui *et al.* [4] also propose that Zn vapour is the condensing species. This path is also suggested by Borchers *et al.* [5] in their paper describing the impact of catalyst-nanostructure interaction in ZnO nanostructure growth. In a paper discussing pulsed laser deposited ZnO films, Im *et al.* [6] suggest a combination of (i) Zn vapour condensation with later oxidation and (ii) ZnO molecular condensation, with the dominant one being dependent on experimental conditions.



Figure 3.2: Possible paths to formation of ZnO(s):(a)Condensation of Zn vapour and subsequent oxidation to form ZnO(s), (b)Direct condensation of ZnO vapour to ZnO(s) (adapted from reference [6])

We examine the thermodynamics of the two possible paths (a) Zn(g) condensation followed by oxidation and (b) ZnO(g) condensation to crystalline ZnO. Figure 3.2 illustrates these two options. To begin, we examine option (a), where Zn vapour condensation onto the substrate is followed by oxidation forming ZnO(s).

This chapter describes the thermodynamic methods used to calculate the amount of Zn vapour generated by CTR of ZnO powder and the saturation of the Zn vapour present in the growth chamber. First, using the Gibbs free energy to calculate exactly how much Zn vapour is generated by the CTR reaction, we find the partial pressure of the Zn vapour produced. We then determine the saturation of this vapour and how likely it is to condense on the substrate surface. Using the calculated partial pressure, we find the impingement rate of Zn molecules on to a growing ZnO nanowire. This value is compared to the observed experimental value.

# 3.2 The Gibbs free energy of reaction for the carbothermal reduction of ZnO

The first stage of VPT growth involves the generation of the source species, Zn, via the CTR of ZnO powder. Carbon acts as a reducing agent of ZnO powder to produce Zn vapour. The Gibbs free energy of a system measures the amount of non-expansive work that can be obtained from that system. The change in Gibbs free energy when a reaction takes place at constant pressure and volume, gives the maximum non expansive work available from that reaction. Reactions with a decreasing Gibbs free energy of reaction will spontaneously occur whereas if the Gibbs free energy is increasing then the reverse reaction will be spontaneous. The Gibbs free energy of the CTR reactions can be found using standard thermodynamic data (eg. from the IVANTHERMO [7] database). There are two possible reactions for the CTR of ZnO powder. We plot the Gibbs free energy of the possible CTR reactions to identify which reaction will occur. The lower the Gibbs free energy of reaction product for the two possible reactions, at a particular temperature, the more likely the occurrence of the reaction.

The Gibbs free energy of reaction ( $\Delta G_r$ ) for each of the two possible CTR reactions indicated in Equation 3.1 are shown in Figure 3.3. For both reactions  $\Delta G_r$ decreases with increasing temperature showing that the reaction is more likely to proceed as the temperature increases. As can be seen from the plot, the reactions that describe the CTR of ZnO powders in the low (T < 973K) and high (T > 973K) temperature regime can be identified as:

$$T < 973 \text{ K} \quad \text{ZnO}(s) + \frac{1}{2}\text{C}(s) \rightarrow \text{Zn}(g) + \frac{1}{2}\text{CO}_2(g)$$
(3.1)  
$$T > 973 \text{ K} \quad \text{ZnO}(s) + \text{C}(s) \rightarrow \text{Zn}(g) + \text{CO}(g)$$



Figure 3.3: Gibbs free energy of reaction for CTR of ZnO as a function of temperature

In our growth system the CTR reaction takes place at 1200 K, therefore for our calculations we take the reaction with lower value of the Gibbs free energy of reaction at that temperature, the reaction generating CO(g).

# 3.3 The saturation of Zn vapour

# 3.3.1 Calculation of the partial pressure of Zn vapour

We find the equilibrium constant  $(K_p)$  of a reaction using the Gibbs free energy of the reaction  $(\Delta G_r)$  [8] :

$$K_{p} = \exp\left(\frac{-\Delta G_{r}}{RT}\right)$$
(3.2)

Using the Gibbs free energy of the CTR reactions, we establish the equilibrium constant. For a reaction  $n_1A(g) + n_2B(g) \rightarrow n_3C(g)$ , the equilibrium constant is given by:

$$K_{p} = \frac{\left(\frac{P_{C}}{P_{\ominus}}\right)^{n_{3}}}{\left(\frac{P_{A}}{P_{\ominus}}\right)^{n_{1}} \left(\frac{P_{B}}{P_{\ominus}}\right)^{n_{2}}}$$
(3.3)

Where  $P_A$ ,  $P_B$  and  $P_C$  are the partial pressures of the gaseous species A(g), B(g) and C(g) and where  $P_{\ominus}$  is 1 bar. Similarly for the reactions in Equation 3.1 we find:

$$T < 973K \quad K_{p} = \left(\frac{P_{Zn}}{P_{\ominus}}\right) \left(\frac{P_{CO_{2}}}{P_{\ominus}}\right)^{\frac{1}{2}}$$
(3.4)  
$$T > 973K \quad K_{p} = \left(\frac{P_{Zn}}{P_{\ominus}}\right) \left(\frac{P_{CO}}{P_{\ominus}}\right)$$

Using the equilibrium constant,  $K_p$ , calculated by Equation 3.2 we calculate the partial pressure of the Zn vapour. The partial pressure of Zn is normalized, so that the total partial pressure of all gases present in the furnace tube (the sum of the partial pressures of the Ar, CO/CO<sub>2</sub>,O<sub>2</sub> and Zn vapours) remains at one atmosphere pressure, because the tube is open to the external atmosphere, via the exhaust line.

The equilibrium vapour pressure is the pressure of a vapour in thermodynamic equilibrium, with its condensed phase, in a closed system. It is the pressure at which the vapour will condense. The vapour pressure of Zn was calculated using the Gibbs free energy of the phase change  $Zn(g) \rightarrow Zn(c)$  using standard thermodynamic values [7]. Zn(c) refers to condensed-phase Zn. At temperatures below 692 K [9], this phase will be solid, and above 692 K it will be liquid. The equilibrium constant



Figure 3.4: Illustration of the condensation of Zn vapour,  $Zn(g) \rightarrow Zn(c)$ 

 $(K_p)$  and equilibrium vapour partial pressure are determined from the Gibbs free energy of the reaction  $Zn(g) \rightarrow Zn(c)$ . This gives the equilibrium pressure of Zn vapour over condensed Zn, the pressure at which Zn(g) will form condensed-phase Zn(c),

$$\exp\left(\frac{-\Delta G_{\rm r}}{\rm RT}\right) = \frac{\rm VP_{Zn}}{\rm P_{\ominus}} \tag{3.5}$$

where  $VP_{Zn}$  is the equilibrium vapour pressure of Zn. The calculated partial pres-



Figure 3.5: The partial pressure and vapour pressure of Zn vapour produced by the CTR of ZnO powder as a function of temperature

sures and vapour pressures of Zn are shown in Figure 3.5 as a function of temperature over the temperature range of interest for VPT. The value of the partial pressure of the Zn vapour is the maximum possible value. In reality, other experimental factors such as the degree of mixing of the ZnO powder and graphite as well as issues around the transport of vapour from source to substrate will reduce the amount of Zn vapour produced. The partial pressure of the Zn vapour increases with increasing temperature until it reaches a limiting value of 0.5 atm. This is the maximum value that the Zn vapour can reach as the total pressure of the furnace is 1 atm. The partial pressure of Zn, at the growth temp of 1200 K, is 0.294 atm. The vapour pressure at this temperature is 1.201 atm.
#### 3.3.2 The degree of saturation of Zn vapour

The condensation of Zn vapour on to the substrate is a phase transition. The direction of a phase transition is such that it will reduce the energy of a system. If two phases (a and b) are not in equilibrium, the force that drives the system towards equilibrium is the difference between the chemical potential of each phase [10].

$$\Delta \mu = \mu_{\rm a} - \mu_{\rm b} \tag{3.6}$$

The chemical potential of a phase  $(\mu)$  is the amount by which the Gibbs free energy of the phase would change if an additional amount of material (n) was introduced, with the pressure and temperature held fixed. It can be expressed in terms of the partial pressure of that phase.

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{P,T} = RT \ln P \tag{3.7}$$

Where P is the pressure of the vapour, T is the absolute temperature and R is the ideal gas constant. The difference in the chemical potential is given by:

$$\Delta \mu = \operatorname{RT} \ln \frac{P_{a}}{P_{b}} \tag{3.8}$$

If the pressure ratio  $\frac{P_a}{P_b}$  is > 1,  $\Delta \mu$  is positive, driving an increase in the amount of molecules in phase a. If the ratio is < 1,  $\Delta \mu$  is negative and the number of molecules in phase b will increase.

Equation 3.8 can be rewritten as:

$$\Delta \mu = \operatorname{RT} \ln[s+1] \tag{3.9}$$

where the degree of saturation s is:

$$s = \frac{P_a - P_b}{P_b} \tag{3.10}$$

In our case the two phases refer to Zn vapour and condensed phase Zn. The degree of saturation indicates whether a vapour is undersaturated (s <1) or supersaturated (s >1), corresponding to whether its partial pressure is less than or greater than the equilibrium vapour pressure at that temperature. The degree of saturation determines whether a molecule that condenses onto the surface remains on the surface ultimately contributing to a growing crystallite, or whether it evaporates back to the vapour state. The degree of saturation of Zn vapour is given by:

$$s = {p - p_0 \over p_0}$$
 (3.11)

where p is the partial pressure of the vapour and  $p_0$  is the equilibrium vapour pressure. Figure 3.6 shows the degree of saturation of Zn vapour over condensed Zn. The vapour pressure is the pressure of the vapour over condensed Zn; the saturation of Zn vapour on a bare (no seeds/accommodation sites present) substrate. The degree of saturation increases initially with temperature. This reflects the fact that as the temperature increases, the partial pressure of Zn increases becoming closer to the vapour pressure value. The partial pressure starts to plateau at a limiting value of 0.5 atm at a temperature of ~ 1200 K. The equilibrium vapour pressure continues to increase with temperature leading to a decrease in the degree of saturation.

The Zn vapour over condensed Zn is undersaturated at all temperatures. A negative value for the degree of saturation indicates there are more molecules leaving the surface than arriving. This result agrees with experimental results shown in Figure 3.7 that there is no nanostructure growth observed on bare (unseeded)  $Si/SiO_2$  substrates. The Zn atoms are unlikely to remain on the substrate long enough to form ZnO; this is problematic when we consider nanowires grown on seeded substrate.



Figure 3.6: Degree of saturation for Zn(g) over condensed phase Zn as a function of temperature



Figure 3.7: SEM image of nanostructure growth showing no growth on bare/unseeded  $Si/SiO_2$  substrate

# 3.3.3 Alternative definition of the vapour pressure of Zn vapour

To address the problems presented by the results of the previous section we must look at a different definition of the vapour pressure of the Zn vapour. An alternate definition of vapour pressure in this situation calculates the vapour pressure of Zn over solid ZnO, finding the pressure at which Zn vapour and oxygen will form solid ZnO. Once a nanowire has started growing (i.e the substrate is solid ZnO) this would be the relevant Zn 'vapour pressure'. This is calculated from the Gibbs free energy of the reaction  $Zn(g) + \frac{1}{2}O_2 \rightarrow ZnO(s)$ , with  $P_{O_2} = \frac{1}{2}P_{Zn}$  are then,

$$\exp\left(\frac{-\Delta G_{\rm r}}{\rm RT}\right) = \frac{(\rm VP_{Zn})^{\frac{2}{3}}}{\sqrt{2}P_{\ominus}}$$
(3.12)

Where  $\mathrm{VP}_{\mathrm{Zn}}$  is the equilibrium vapour pressure of Zn.



Figure 3.8: Illustration of reaction  $\rm ZnO(s) \rightarrow Zn(g) + \frac{1}{2}O_2$ 



Figure 3.9: The degree of saturation of Zn vapour over solid ZnO as a function of temperature

Figure 3.9 shows the degree of saturation of Zn vapour over solid ZnO, i.e the saturation of Zn over an existing nanowire crystal. The Zn vapour over solid ZnO is supersaturated at all temperatures and is 422 at the growth temperature of 1200 K. This suggests that once a ZnO nanowire has started to grow, Zn vapour will readily

condense (and remain) on the nanowire and oxidise to form ZnO(s).

#### 3.4 The impingement rate of Zn atoms

To confirm that our calculations are in general agreement with experimental results, we calculate how many molecules are required to produce the nanowires we observe. This is estimated by assuming an average density of 25 nanorods/ $\mu$ m<sup>2</sup> of length 2  $\mu$ m and diameter 75 nm over a growth time of one hour at a growth temperature of 1200 K, as observed on a typical sample of ZnO nanowires grown via VPT. The estimated impingement rate required to produce nanowires of these dimensions and densities is  $2.4 \times 10^{18}$  molecules/m<sup>2</sup>s.

The impingement rate of atoms/molecules from a vapour can be calculated from the partial pressure of that vapour using the Knudsen relation [11]:

$$J = \frac{p}{\sqrt{2\pi m k_b T}}$$
(3.13)

Where p is the partial pressure of the species. Using the partial pressures for Zn and  $O_2$ , we calculate the impingement rate. The partial pressure for  $O_2$  is calculated from the relative value in the gas flow mix. The sticking coefficient  $\alpha_{Zn}$  for Zn is assumed to be unity. The sticking coefficient for oxygen is not unity, as it is a diatomic molecule, and the dissociation of oxygen molecules to react with Zn atoms is a complex process. We find the sticking coefficient  $\alpha_{O_2}$  using an expression derived by Carlos Rojo *et al.* [12]

$$\alpha_{O_2} = (0.27966) \exp\left[\frac{-14,107.9578}{T}\right]$$
(3.14)

For completeness also shown in Figure 3.10 is the net impingement rate of Zn atoms.

Net Rate = 
$$J_{Zn}$$
 condensed -  $J_{Zn}$  evaporation (3.15)

This equilibrium vapour pressure of Zn vapour over solid ZnO is used to find the rate at which molecules are leaving the substrate. As is shown, once the wire has started to grow, the number of molecules leaving the surface does not alter the overall rate except at temperatures higher than those used in our growth system.

The impingement of Zn atoms is quite high, however the number of Zn atoms that will form ZnO is limited by the amount of  $O_2$  arriving at the surface, in order for the Zn atoms to be oxidized to form ZnO and thus determined by  $\alpha_{O_2}J_{O_2}$ . This gives rather good agreement to the observed experimental value. As mentioned previously the partial pressure of the Zn vapour produced calculated is a maximum possible value and will be in reality lower due to experimental factors.



Figure 3.10: Effective impingement rates for Zn and  $O_2$ 

## 3.5 Conclusions

This chapter examines the generation of Zn vapour by CTR in VPT growth of ZnO nanowires. The relevant CTR reactions are identified. We calculate the partial pressure of the Zn vapour produced, using the Gibbs free energy of these reactions. We then compare the partial pressure and the equilibrium vapour pressure to determine the degree of saturation of the Zn vapour.

Calculations of the partial pressures and degree of saturation of Zn vapour over condensed phase Zn show that while the partial pressure of Zn vapour is relatively large, the vapour is undersaturated and so will not condense on the surface unless energetically suitable accommodation sites exist for nucleation to take place.

However, the saturation of Zn vapour over solid ZnO is 422, at a growth tem-

perature of 1200 K (and significantly greater than 1 over a wider temperature range from 600 K to 1600 K), indicating that once the nanostructure has nucleated and started to grow, Zn vapour atoms will readily condense at the ZnO crystallite, and react with  $O_2$  to form ZnO.

These results are consistent with experimental evidence, which shows that ZnO nanowires do not grow on bare substrates as Zn vapour is undersaturated and does not condense in these areas without accommodation sites. The values for the degree of saturation over an already growing nanowire show that, once nucleation has taken place, Zn vapour will contribute to ZnO nanowire growth.

The impingement rates of Zn atoms and  $O_2$  molecules on to a growing nanowire were calculated. These values were compared to an estimation of the observed impingement rate. It was found that the calculated impingement rate was sufficient to account for the observed nanowire growth.

# Bibliography

- M Kubo, Y Oumi, H Takaba, A Chatterjee, A Miyamoto, M Kawasaki, M Yoshimoto, and H Koinuma. Homoepitaxial growth mechanism of ZnO(0001): Molecular-dynamics simulations. *PHYSICAL REVIEW B*, 61(23):16187–16192, JUN 15 2000.
- [2] Dong Sik Kim, Roland Scholz, Ulrich Goesele, and Margit Zacharias. Gold at the root or at the Tip of ZnO Nanowires: A Model. SMALL, 4(10):1615–1619, OCT 2008.
- [3] S. R. Hejazi and H. R. Madaah Hosseini. A diffusion-controlled kinetic model for growth of Au-catalyzed ZnO nanorods: Theory and experiment. *JOURNAL OF CRYSTAL GROWTH*, 309(1):70–75, NOV 1 2007.
- [4] Kittitat Subannajui, Niranjan Ramgir, Raphael Grimm, Rebecca Michiels, Yang Yang, Stefan Mueller, and Margit Zacharias. ZnO Nanowire Growth: A Deeper Understanding Based on Simulations and Controlled Oxygen Experiments. CRYSTAL GROWTH & DESIGN, 10(4):1585–1589, APR 2010.
- [5] C Borchers, S Muller, D Stichtenoth, D Schwen, and C Ronning. Catalystnanostructure interaction in the growth of 1-D ZnO nanostructures. *JOURNAL* OF PHYSICAL CHEMISTRY B, 110(4):1656–1660, FEB 2 2006.

- S Im, BJ Jin, and S Yi. Ultraviolet emission and microstructural evolution in pulsed-laser-deposited ZnO films. JOURNAL OF APPLIED PHYSICS, 87(9, Part 1):4558–4561, MAY 1 2000.
- [7] values **IVANTHERMO** database Glushko Therused in by of Russian Academy Sciences listed mocenter the of at http://www.chem.msu.su/rus/tsiv/Zn/table.Zn.6.html.
- [8] P.W Atkins. *Physical Chemistry*. Oxford, 1998.
- [9] M.W. Chase, editor. NIST-JANAF Thermochemical Tables, 4th ed. American-Chemical Society, American Institute of Physics for the National Institute of Standards and Technology, Woodbury, N.Y., 1998.
- [10] I.V Markov. Crystal Growth for Beginners, 2nd edition. World Scientific, London, 2003.
- [11] Donald L. Smith. Thin-Film Deposition, Principles and Practice. McGraw-Hill, 1995.
- [12] J. C. Rojo, S. Liang, H. Chen, and M. Dudley. Physical vapor transport crystal growth of ZnO. In F. Hosseini Teherani & C. W. Litton, editor, Society of Photo-Optical Instrumentation Engineers (SPIE) Conference Series, volume 6122 of Society of Photo-Optical Instrumentation Engineers (SPIE) Conference Series, pages 97–104, March 2006.

# Chapter 4

# Thermodynamic analysis of ZnO vapour

#### 4.1 Introduction

This chapter describes the calculation of the partial pressure and degree of saturation of ZnO vapour present during growth in the furnace chamber. We study the thermodynamics of the formation and condensation of ZnO vapour.

The first step is to calculate the relative amount or partial pressure of the ZnO vapour present in the furnace. To do this we need to examine the thermodynamics of the reaction  $\operatorname{Zn}(g) + \frac{1}{2}O_2(g) \to \operatorname{ZnO}(g)$ . Finding the Gibbs free energy of the reaction requires us to calculate the Gibbs free energy of each species. Ordinarily, the Gibbs free energy of a molecule can be found in tables of thermochemical data [1,2]. In the case of the ZnO gaseous molecule, there is some debate about the various relevant parameters of the molecule, thus there is no definitive value for the Gibbs free energy of the ZnO(g) vapour we derive a model to find the thermodynamic variables for a diatomic model, assuming that the monatomic and diatomic molecules; this

is applicable in our experimental situation, as the temperature is high enough that the thermal energy of the molecules will exceed the inter-molecular energy. We use the Gibbs free energy of the reaction  $\operatorname{Zn}(g) + \frac{1}{2}O_2(g) \to \operatorname{ZnO}(g)$  to find the partial pressure of ZnO vapour, which we compare with the vapour pressure of ZnO vapour to predict the likelihood of condensation.



Figure 4.1: Illustration of the formation and condenstation of ZnO(g)

#### 4.2 ZnO gaseous molecule

The thermodynamic calculations in this thesis require parameters for the diatomic gaseous molecule ZnO, such as internuclear distance  $r_e$ , the vibrational frequency  $\nu_0$ , the dissociation energy  $D_0$  and the difference in energy between the first excited electronic state and the energy of the ground state  $\Delta \epsilon$ . Figure 4.2 illustrates the parameters  $D_0$  and  $r_e$  on a plot of potential energy as a function of internuclear distance. The dissociation energy is the energy of the chemical bond between the two atoms. The figure shows both  $D_e$  and  $D_0$ , where  $D_e = D_0 + \frac{1}{2}h\nu_0$ .  $D_e$  is the actual depth of the potential well but even at T = 0 K, the molecule will have an energy of  $\frac{1}{2}h\nu_0$  in its lowest vibrational state.  $D_0$  is the energy that would be required to dissociate the molecule into two atoms at T = 0 K. The internuclear distance,  $r_e$ is the equilibrium value of r for which the potential energy of the molecule is at a minimum. Despite the relative dearth of experimental evidence for the existence and properties of this molecule, there are various reported values for these parameters.



Figure 4.2: Potential energy of a diatomic molecule as a function of internuclear distance r: showing equilibrium distance  $r_e$ , dissociation energy  $D_0$ , and the vibrational energy levels, adapted from [3]

The molecular parameters of the ZnO(g) molecule were first studied by Brewer and Chandrasekharaiah [4], whose technical report on gaseous monoxides estimated values of  $r_e$  and  $\nu_0$ , respectively as 1.74 Å and  $2.0385 \times 10^{13}$  Hz (based on extrapolation from neighbouring species). These values have been refined over the years and compared with various theoretical measurements, and the current best estimates for  $r_e$  and  $\nu_0$  are 1.72 Å and 2.33828 × 10<sup>13</sup> Hz, respectively [2].

The value of the dissociation energy,  $D_0$ , has been continuously revised. Brewer and Mastick [5] studied the rate of vapourization of several diatomic oxides, finding that ZnO sublimes by decomposition into Zn and O<sub>2</sub>. Brewer and Mastick found no direct evidence of the ZnO gaseous molecule, they set an upper limit on  $D_0$  of 3.99 eV based on the threshold of detection. Anthrop and Searcy [6] investigated the sublimation of ZnO by Knudsen weight loss measurements with mass spectroscopy of the resulting vapours; they did not detect gaseous ZnO and gave an upper limit on  $D_0$  of and 2.86 eV based on the sensitivity of the mass spectrometer. Grade et al. [7] claim to have found evidence of the existence of the gaseous ZnO molecule; they measured a value of 2.91 eV for  $D_0$ . Clemmer, Dalleska and Armentrout [8] determined a value of 1.61 eV for  $D_0$  using guided ion-beam mass spectroscopy. Watson et al. [9] again did not observe gaseous ZnO, but based on spectrometer sensitivity, refined the upper limit to 2.3 eV. Bauschlicher and Partridge performed ab inito electronic structure calculations, which found a value for  $D_0$  of 1.63 eV [10]. Calculations by Gusarov and Iorish found a value of 1.77 eV [11], which is used in the most recent version of the IVTANTHERMO database [2]. For our calculations four different sets of parameters were used.

# 4.3 A model to calculate the Gibbs free energy of a diatomic molecule

A basic model of a diatomic ideal gas was used to calculate the Gibbs free energy of the reaction  $\operatorname{Zn}(g) + \frac{1}{2}O_2(g) \to \operatorname{ZnO}(g)$ . The model assumes the gas consists of N identical non-interacting molecules. The energy of a diatomic molecule can be expressed as a sum of contributions to the total energy [3]:

$$E_{\text{total}} = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{electronic}}$$
(4.1)

The probability of a particle being in a state n is given in terms of the partition function.

$$P_n = \frac{e^{-\beta E_n}}{Z}$$
(4.2)

Where Z is the canonical partition function, given by,

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n}$$
(4.3)

and where  $\beta = \frac{1}{k_b T}$  and  $E_n$  is the energy of the state n. The partition function (so named because it details how energy is partitioned among the states of a system) can be used to find most of the thermodynamic variables of the system, such as the free energy F, the helmholtz free energy H and the Gibbs free energy G. The

partition function for a single diatomic molecule, z is defined as [12]:

$$z = \exp(-\beta E_{\text{total}}) \tag{4.4}$$

(4.5)

with,

$$z = \exp(-\beta(E_{trans})\exp(-\beta E_{rot})\exp(-\beta E_{vib})\exp(-\beta E_{elec})$$

$$z = z_{tran} z_{rot} z_{vib} z_{elec}$$
(4.6)



Figure 4.3: A diatomic molecule

### 4.3.1 Translational contribution to the partition function

The diatomic molecule consists of two masses m1 and m2 as illustrated in Figure 4.3. In calculating the translational contribution to the partition function the diatomic molecule is taken to be a single particle of mass  $m = m_1 + m_2$ . The partition function is given by [12]:

$$z = \sum_{n} \exp(-\beta \epsilon_{n})$$
(4.7)

The energy levels for this particle are found by solving the Schrödinger equation for a particle in a three dimensional infinite potential well (i.e a box). The energy levels are given by:

$$\epsilon_{\rm n} = \frac{\hbar^2}{2\mathrm{m}} \left(\frac{\pi}{\mathrm{L}}\right)^2 \left(\mathrm{n}_{\rm x}^2 + \mathrm{n}_{\rm y}^2 + \mathrm{n}_{\rm z}^2\right) \tag{4.8}$$

Where L is the width of the potential well,  $n_x, n_y, n_z$  are integers, m is the mass of the molecule and  $\hbar^2 = h/2\pi$  is the reduced Planck's constant. This gives:

$$z \simeq \int \int \int dn_x dn_y dn_z \exp\left(\frac{\hbar^2 \beta}{2m} \left(\frac{\pi}{L}\right)^2 \left(n_x^2 + n_y^2 + n_z^2\right)\right)$$

$$\simeq \left(\int dn_x \exp\left(\frac{\hbar^2 \beta}{2m} \left(\frac{\pi}{L}\right)^2 \left(n_x^2\right)\right)^3$$
(4.9)

The translational contribution to the partition function is:

$$z_{\rm trans} = V \left(\frac{mk_{\rm b}T}{2\pi\hbar^2}\right)^{\frac{3}{2}} = \frac{V}{\lambda_{\rm T}}^3$$
(4.10)

with V = l<sup>3</sup>. The thermal wavelength is given by  $\lambda_{\rm T} = \hbar \left( \frac{2\pi}{k_{\rm bTm}} \right)$ .

# 4.3.2 Rotational contribution to the partition function

The rotational contribution to the partition function is calculated by assuming the diatomic molecule to be a rigid dumbbell that can rotate about an axis through the centre of mass of the molecule as illustrated in Figure 4.4.

For one diatomic molecule the contribution to the rotational partition function is given by [12]:

$$z = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \exp\left(-\beta \epsilon_{l,m}\right)$$
(4.11)

The energy of a rotating molecule is given by [13]:

$$E = \frac{L^2}{2I} \tag{4.12}$$

where I is the moment of inertia of the molecule and L is the total angular momentum. The angular momentum is quantized:  $L^2 = l(l+1)\hbar^2$  with l = 0, 1, 2, 3...



Figure 4.4: Rotational motion of diatomic molecule

The energy levels for a rotating diatomic molecule are:

$$\epsilon_{l,m} = \frac{\hbar^2 l \, (l+1)}{2I} \tag{4.13}$$

and I is the moment of inertia of the diatomic molecule where  $I = \left(\frac{m_1 m_2}{m_1 + m_2}\right) R^2$ , where R is the distance between the centres of the atoms in the diatomic molecule.

$$z = \sum_{l=0}^{\infty} \exp\left(-\frac{\beta\hbar^2 l(l+1)}{2I}\right) \left(\sum_{m=-l}^{l} 1\right)$$

$$= \sum_{l=0}^{\infty} (2l+1) \exp\left(-\frac{\beta\hbar^2 l(l+1)}{2I}\right)$$
(4.14)

If  $k_{\rm b}T\gg \frac{\hbar^2}{2I}$  we can replace the sum with an integral:

$$z = \int_0^\infty dl \left(2l+1\right) \exp\left(-\frac{\beta \hbar^2 l \left(l+1\right)}{2I}\right)$$
(4.15)

which can be written as:

$$z = -\int_0^\infty dl \left(\frac{2I}{\beta\hbar^2} \frac{\partial}{\partial l} \left[\exp\left(-\frac{\beta\hbar^2 l \left(l+1\right)}{2I}\right)\right]$$
(4.16)

$$z = \frac{2I}{\beta\hbar^2} \tag{4.17}$$

and we need to write,

$$z = \frac{2I}{\beta\hbar^2\sigma} \tag{4.18}$$

where  $\sigma$  is the symmetry number of the diatomic molecule. For a symmetric molecule,  $O_2 \ \sigma = 2$  for a non symmetric molecule ZnO,  $\sigma = 1$ . The symmetry number addresses the fact that for symmetric molecules, there are two indistinguishable configurations. The number of states for a symmetric molecule would be over counted by a factor of two unless we divide by the symmetry number. The rotational contribution to the partition function is:

$$z_{\rm rot} = \frac{k_{\rm b}T}{{\rm hcB}\sigma} = \frac{T}{\sigma\theta_{\rm R}}$$
(4.19)

where the rotational constant  $B = \frac{\hbar}{4\pi cI}$  and the characteristic temperature for rotation is  $\theta_R = \frac{hcB}{k_b}$ . Note the condition to replace the sum with the integral above can be written as  $T >> \theta_R$ .

#### 4.3.3 Vibrational contribution to the partition function

The molecule is taken to consist of two particles of masses  $m_1$  and  $m_2$  connected by a spring as shown in Figure 4.5. The vibrational contribution to the partition function for one molecule:

$$z = \sum_{n=0}^{\infty} \exp(-\beta\epsilon_n)$$
(4.20)



Figure 4.5: Vibrational motion of diatomic molecule

The potential energy of the bond between the molecules can be approximated by a harmonic potential,  $V(R) = \frac{1}{2}kR^2$  as illustrated in Figure 4.6. Though the thermal energy in our experimental situation is quite high (~  $1.65 \times 10^{-20}$  J) the dissociation energy of the ZnO molecule is much higher (~  $2.83 \times 10^{-19}$  J) so the approximation is valid even at our high growth temperature.



Figure 4.6: Potential energy of a diatomic molecule approximated as a parabolic function

The energy levels for a quantum harmonic oscillator are given by [13]:

$$\epsilon_{\rm n} = \hbar\omega \left({\rm n} + \frac{1}{2}\right) \tag{4.21}$$

where n = 0, 1, 2, 3.... and,

$$z = \sum_{n=0}^{\infty} \exp\left(-\beta\hbar\omega\left(n+\frac{1}{2}\right)\right)$$

$$= \exp\left(-\frac{\beta\hbar\omega}{2}\right) \sum_{n=0}^{\infty} \exp\left(-n\beta\hbar\omega\right)$$

$$(4.22)$$

The vibrational contribution to the partition function is:

$$z_{\rm vib} = \frac{\exp\left(-\frac{\beta\hbar\omega}{2}\right)}{1 - \exp\left(-\beta\hbar\omega\right)} = \frac{\exp\left(-\frac{\theta_{\rm v}}{2\rm T}\right)}{1 - \exp\left(-\frac{\theta_{\rm v}}{\rm T}\right)} \tag{4.23}$$

Where the characteristic vibrational temperature  $\theta_{\rm V} = \frac{hc\nu_0}{k_{\rm b}}$ .

# 4.3.4 Electronic contribution to the partition function

The electronic contribution to the partition function for one molecule is:

$$z = \sum_{j=0}^{\infty} g_j \exp\left(-\beta \epsilon_j\right)$$
(4.24)

Where  $\epsilon_j$  is the energy of the excited electronic states and  $g_j$  is the degeneracy of the excited electronic states [3].

$$z = g_0 \exp(-\beta\epsilon_0) + g_1 \exp(-\beta\epsilon_1)$$
(4.25)

$$\epsilon_0 = -\mathbf{D}_e = -\mathbf{D}_0 - \frac{1}{2}\hbar\omega \tag{4.26}$$

$$\epsilon_1 = -\mathbf{D}_{\mathbf{e}} + \Delta \epsilon \tag{4.27}$$

$$z_{\text{elec}} = \exp(\beta D_{e}) \left( g_{0} + g_{1} \exp(-\beta \Delta \epsilon) \right)$$
(4.28)

# 4.3.5 The Gibbs free energy

The partition function for a single diatomic molecule z is:

$$z = V\left(\frac{\mathrm{m}k_{\mathrm{b}}T}{2\pi\hbar^{2}}\right)^{\frac{3}{2}} \left(\frac{\mathrm{k}_{\mathrm{b}}T}{\mathrm{h}\mathrm{c}\mathrm{B}\sigma}\right) \left(\frac{\exp\left(-\frac{\beta\hbar\omega}{2}\right)}{1-\exp\left(-\beta\hbar\omega\right)}\right)$$

$$\times \left(\mathrm{g}_{0}\exp\beta\left(\mathrm{D}_{0}+\frac{1}{2}\hbar\omega\right)+\mathrm{g}_{1}\exp\left(-\beta\epsilon_{1}\right)\right)$$

$$(4.29)$$

For N identical diatomic molecules the partition function Z is:

$$Z = \frac{z^N}{N!} \tag{4.30}$$

The free energy is given by [14]:

$$\mathbf{F} = -\mathbf{k}_{\mathbf{b}} \mathbf{T} \ln \mathbf{Z} \tag{4.31}$$

$$F = -Nk_bT + Nk_bT \ln\left(\frac{N}{V}\left(\frac{2\pi\hbar^2}{mk_bT}\right)^{\frac{3}{2}}\right) + Nk_bT \ln\left(\frac{hcB\sigma}{k_bT}\right)$$

$$+\mathrm{Nk}_{\mathrm{b}}\mathrm{T}\ln\left(1-\exp\left(-\beta\hbar\omega\right)\right)-\mathrm{ND}_{0}-\mathrm{Nk}_{\mathrm{b}}\mathrm{T}\ln\left(\mathrm{g}_{0}+\mathrm{g}_{1}(\exp-\beta\Delta\epsilon)\right) \quad (4.32)$$

The Gibbs free energy is given by:

$$G = F - V \left(\frac{\partial F}{\partial V}\right)_{T}$$
(4.33)

$$G = \operatorname{RT} \ln \left[ \left( \frac{p \lambda_{\mathrm{T}}^{3}}{k_{\mathrm{bT}}} \right) \left( \frac{\theta_{\mathrm{R}} \sigma}{\mathrm{T}} \right) \left( 1 - \exp \left( -\frac{\theta_{\mathrm{V}}}{\mathrm{T}} \right) \right) \right]$$
$$-\operatorname{RT} \ln \left[ \sum_{i} g_{i} \exp \left( \frac{-\Delta \epsilon_{i}}{(k_{\mathrm{b}})\mathrm{T}} \right) \right] - \mathrm{D}_{0}$$
(4.34)

with 
$$\lambda_T = \hbar \left(\frac{2\pi}{k_b Tm}\right)$$
  $\theta_R = \frac{hcB}{k_b}$   $B = \frac{\hbar}{4\pi cI}$   $\theta_V = \frac{hc\nu_0}{k_b}$ 

# 4.3.6 Testing the model

We tested this model by calculating the Gibbs free energy and other thermodynamic variables for molecules for which the thermochemical data is widely available [1]. The thermodynamic variable generally listed for molecules is the Gibbs energy function (gef) which is given by:

$$gef(T) = \frac{G(T) - H(T_R)}{T}$$

$$(4.35)$$

Where  $T_R$  is room temperature and the enthalpy H is given by:

$$H(T) = \frac{7}{2}RT + R\theta_{V} \left[ \frac{1}{\exp\left(\frac{\theta_{V}}{T}\right) - 1} \right] + \frac{R\Delta\epsilon}{k_{b}} \left[ \frac{g_{1}\exp\left(\frac{-\Delta\epsilon}{k_{b}T}\right)}{\sum_{i}g_{i}\exp\left(\frac{-\Delta\epsilon_{i}}{k_{b}T}\right)} \right] - D_{0} (4.36)$$



Figure 4.7: The Gibbs energy function for  $O_2$  as a function of temperature



Figure 4.8: The Gibbs energy function for CO as a function of temperature

As is shown in Figures 4.7 and 4.8 the model is in agreement with available data for both  $O_2$  and CO molecules.

#### 4.4 Values used in model

#### 4.4.1 ZnO gaseous molecule

In our calculations we use four different parameter sets corresponding to the results of previous studies which represent the range of values available in the literature. These values are summarised in Table 4.1. In much of the subsequent analysis we show the data for sets three and four below, which represent the extreme values of  $D_0$ , and since  $D_0$  is a key parameter in determining issues around nucleation and growth, the presentation of these data represent the range spanned by  $D_0$  in sets one-four.

Set	$r_e(Å)$	wavenumber $(cm^{-1})$	$D_0(eV)$	$\Delta \epsilon (eV)$
Set1 [10]	1.719	727	1.63	0.26
Set2 [15]	1.719	770	1.63	0.305
Set3 [8]	1.719	805	1.61	0.25
Set $[2]$	1.72	780	1.77	0.32

Table 4.1: Reported values for ZnO molecule

The other accepted values used in the calculations are listed in Table 4.2. To find the degeneracy of the electronic energy levels  $(g_i)$  we look at the molecular energy levels which are listed as:

where 
$$\Lambda = 0, 1, 2, \dots = \Sigma, \Pi, \Delta, \dots$$
 (4.37)

 $\Lambda$  is the quantum number of the molecular energy level and s is the total spin quantum number [16]. For these electronic levels, the degeneracy of each level is given by:

$$g = (2s+1) \times 2 \quad \text{if} \quad \Lambda \neq 0 \tag{4.38}$$
$$g = (2s+1) \times 1 \quad \text{if} \quad \Lambda = 0$$

The degeneracy of the ground state of ZnO,  ${}^{1}\Sigma$  is  $g_{0} = 1$ . The degeneracy of the first excited state,  ${}^{3}\Pi$  is  $g_{1} = 6$ .

Parameter	Unit	Value
$m_1 [1]$	a.m.u	31.99
$m_1 \ [1]$	a.m.u	65.38
$\sigma$	NA	1
$g_0$	NA	1
$g_1$	NA	6

Table 4.2: General values for ZnO molecule used in calculations

## 4.4.2 O<sub>2</sub> gaseous molecule

The data for the  $O_2$  molecule can be found in thermochemical tables [1, 17]. The values used in the model are summarized in Table 4.3. The degeneracy of the ground state of  $O_2$ ,  ${}^3\Sigma$  is  $g_0 = 3$ . The degeneracy of the first excited state,  ${}^1\Delta$  is  $g_1 = 2$ .

Parameter	Unit	Value
$m_1 [1]$	a.m.u	15.99
$m_1 [1]$	a.m.u	15.99
$R_e$ [17]	Å	1.20752
$\nu_0  [1]$	$\mathrm{cm}^{-1}$	1580.1932
$\Delta \epsilon \ [1]$	eV	0.978
$D_0 [1]$	(eV)	5.14
$\sigma$	NA	2
$g_0$	NA	3
$g_1$	NA	2

Table 4.3: Values for  $O_2$  molecule used in calculations

# 4.5 The saturation of ZnO vapour

# 4.5.1 Calculation of the Gibbs free energy of reaction for the formation of ZnO vapour

ZnO vapour in the furnace is produced via the reaction:  $Zn(g) + \frac{1}{2}O_2(g) \rightarrow ZnO(g)$ . The Gibbs free energy of which is given by:

$$\Delta G_{\rm r} = G_{\rm ZnO} - \frac{1}{2} G_{\rm O_2} - G_{\rm Zn}.$$
(4.39)

 $\Delta G_r$  was calculated for ZnO, Zn and O<sub>2</sub>, using the above model of basic ideal monatomic and diatomic gases and the molecular parameters for ZnO(g) summarized in Table 4.1.

For diatomic ZnO and O<sub>2</sub>:

$$G(T)_{ZnO,O_{2}} = RT \ln \left[ \left( \frac{p\lambda_{T}^{3}}{k_{b}T} \right) \left( \frac{\theta_{R}\sigma}{T} \right) \left( 1 - \exp \left( -\frac{\theta_{V}}{T} \right) \right) \right]$$
$$-RT \ln \left[ \sum_{i} g_{i} \exp \left( \frac{-\Delta\epsilon_{i}}{(k_{b})T} \right) \right] - D_{0}$$
(4.40)

with 
$$\lambda_T = \hbar \left(\frac{2\pi}{k_b Tm}\right)$$
  $\theta_R = \frac{hcB}{k_b}$   $B = \frac{\hbar}{4\pi cI}$   $\theta_V = \frac{hc\nu_0}{k_b}$ 

where I is the principal moment of inertia of the molecule,  $D_0$  is the dissociation energy,  $\nu_0$  is the vibration frequency,  $r_e$  is the interatomic distance,  $\Delta \epsilon_i$  is the difference in energy between the i<sup>th</sup> excited state and the energy of the ground state,  $g_i$  is the degeneracy of the excited electronic states, m is the molecular mass and R, c, h,  $\hbar$ ,  $k_b$  have their usual meanings [1].

For monatomic Zn(g):

$$G(T) = RT \ln \left[ \frac{p \lambda_{T}^{3}}{k_{b} T} \right]$$
(4.41)
with  $\lambda_{T} = \hbar \left( \frac{2\pi}{k_{b} T m} \right)$ 

where m is the mass of atomic Zn.



Figure 4.9:  $\Delta G_r$  for reaction  $Zn(g) + \frac{1}{2}O_2(g) \rightarrow ZnO(g)$  as a function of temperature

Figure 4.9 shows the Gibbs free energy of reaction  $\Delta G_r$  for each parameter set from Table 4.1 as a function of temperature over the temperature range of interest for VPT, from 300 K to 2000 K.  $\Delta G_r$  for the generation of ZnO is positive for all temperatures. This indicates that the production of ZnO vapour is not energetically favourable.  $\Delta G_r$  increases with increasing temperature. The values for  $\Delta G_r$  vary for each set of parameters used, depending mainly on the dissociation energy value used in these calculations.

#### 4.5.2 Calculation of the partial pressure of ZnO

The equilibrium constant  $K_p$  for the reaction  $Zn(g) + \frac{1}{2}O_2(g) \rightarrow ZnO(g)$  is found using the Gibbs free energy of the reaction calculated above [16]:

$$K_{p} = \exp\left(\frac{-\Delta G_{r}}{RT}\right)$$
(4.42)

The partial pressure of ZnO is found using:

$$K_{p} = \frac{\left(\frac{p_{ZnO}}{p_{\Theta}}\right)}{\left(\frac{p_{Zn}}{p_{\Theta}}\right)\left(\frac{p_{O_{2}}}{p_{\Theta}}\right)^{\frac{1}{2}}}$$
(4.43)

Using partial pressure of Zn vapour produced by CTR (as calculated in Chapter 3) and that of  $O_2$  as calculated from the relative value in the gas flow mix, we find the partial pressure of ZnO vapour. The partial pressure is normalised so that the total pressure in the furnace remains at 1 atm.

The ZnO(g) vapour pressure, in equilibrium with the ZnO(s) condensed phase, is calculated by determining the Zn(g) and  $O_2(g)$  pressures in equilibrium with a congruently subliming ZnO(s) condensed phase and calculating the ZnO(g) pressure in equilibrium with those Zn(g) and  $O_2(g)$  species.



Figure 4.10: Illustration of the evaporation of ZnO

The Zn vapour pressure is calculated by using the equilibrium constant for the reaction  $\operatorname{Zn}(g) + \frac{1}{2}O_2(g) \to \operatorname{ZnO}(s)$ , which gives the vapour pressure of  $\operatorname{Zn}(g)$  over  $\operatorname{ZnO}(s)$ . This partial pressure, as the input for the equilibrium constant for the reaction  $\operatorname{Zn}(g) + \frac{1}{2}O_2(g) \to \operatorname{ZnO}(g)$ , gives the vapour pressure of  $\operatorname{ZnO}(g)$  over  $\operatorname{ZnO}(s)$ .

The calculated partial pressures and vapour pressures of ZnO are shown in Figure 4.11 as a function of temperature over the temperature range of interest for VPT. The partial pressure of ZnO at a temperature of 1200 K is  $1.73 \times 10^{-7}$  atm. The vapour pressure at this temperature is  $8.83 \times 10^{-16}$  atm. The partial pressure of the ZnO vapour is quite small when compared with the partial pressure of Zn vapour at the same temperature which is 0.29 atm. The partial pressure of ZnO increases with increasing temperature, despite the fact that the Gibbs free energy is increasing. The increase in the partial pressure of the Zn vapour produced by the CTR reaction leads to an increase in ZnO vapour produced.



Figure 4.11: The partial and vapour pressures of ZnO as a function of temperature

## 4.5.3 The degree of saturation of ZnO vapour

The degree of saturation of a vapour is given by:

$$s = \frac{p - p_0}{p_0}$$
 (4.44)

where  $p_0$  is the vapour pressure. Figure 4.12 shows the saturation of ZnO vapour over solid ZnO for two values of molecular parameters (sets 3 and 4 from Table 4.1).



Figure 4.12: The degree of saturation of ZnO vapour as a function of temperature

The pressure of ZnO is far, far greater than the vapour pressure of ZnO, showing that ZnO(g) is supersaturated at all temperatures to a large degree. The degree of saturation of the ZnO vapour at the growth temperature of 1200 K is  $1.99 \times 10^8$ .

#### 4.6 The impingement rate of ZnO molecules

The impingement rate of ZnO molecules is calculated using the Knudsen relation [18]:

$$J = \frac{p}{\sqrt{2\pi m k_b T}} \tag{4.45}$$

Figure 4.13 shows the impingement rates for ZnO. Also shown are the impingement rates for Zn and  $O_2$  calculated in Chapter 3. The observed experimental impinge-
ment rate is estimated by assuming an average density of 25 nanorods/ $\mu$ m<sup>2</sup> of length 2  $\mu$ m and diameter 75 nm over a growth time of one hour at a growth temperature of 1200 K. The estimated impingement rate required to produce nanowires of these dimensions and densities at a growth temperature 1200 K is  $2.4 \times 10^{18}$  molecules/m<sup>2</sup>s.



Figure 4.13: Effective impingement rates for Zn,  $O_2$  and ZnO species as a function of temperature

The impingement rate of ZnO molecules, while smaller than Zn, is still greater than that required for the growth observed at temperatures over 1000 K. This indicates that both species can contribute to the growth of ZnO nanowires in VPT growth via CTR. It is important to note here that the impingement rates are based on the maximum possible production of Zn and ZnO vapour from the CTR of ZnO powder.

#### 4.7 Conclusions

This chapter describes the development and application of a model to calculate the partial pressure of ZnO vapour. The success of the model in calculating the Gibbs free energy of a diatomic molecule is confirmed by comparison with accepted values for oxygen and carbon monoxide [1]. We find the Gibbs free energy of the reaction  $Zn(g) + \frac{1}{2}O_2(g) \rightarrow ZnO(g)$  using this model, it is positive, indicating that a relatively small amount of ZnO(g) is produced. The partial pressure of ZnO vapour is relatively small, compared to Zn vapour partial pressure. The degree of saturation of the ZnO vapour produced is very large (s>> 1 for all temperatures).

The results show that while there is relatively little ZnO vapour present, the vapour is supersaturated to a large degree. We would expect to find that the ZnO present would readily condense on the substrate. This finding does not agree with experimental observations that ZnO nanostructure growth occurs only on suitable accommodation sites, suggesting other barriers to ZnO nucleation.

## Bibliography

- M.W. Chase, editor. NIST-JANAF Thermochemical Tables, 4th ed. American-Chemical Society, American Institute of Physics for the National Institute of Standards and Technology, Woodbury, N.Y., 1998.
- [2] values used in **IVANTHERMO** database by Glushko Therof Russian Sciences mocenter the Academy of listed at http://www.chem.msu.su/rus/tsiv/Zn/table.Zn.6.html.
- [3] Terrell L. Hill. An Introduction to Statistical Thermodynamics. Dover Publications, 1986.
- [4] M.S Brewer, L.; Chandrasekharaiah. Free energy functions for gaseous monoxides. Lawrence Berkeley Radiation Laboratory Report, 1960.
- [5] D.F. Brewer, L.; Mastick. J. Chem. Phys., 19:834, 1951.
- [6] DF Anthrop and AW Searcy. Sublimation + Thermodynamic Properties of Zinc Oxide. JOURNAL OF PHYSICAL CHEMISTRY, 68(8):2335–&, 1964.
- [7] M Grade, W Hirschwald, and F Stolze. Detection and stability of zno molecules in gas-phase. ZEITSCHRIFT FUR PHYSIKALISCHE CHEMIE-FRANKFURT, 100:165–174, 1976.

- [8] CA Fancher, HL de Clercq, OC Thomas, DW Robinson, and KH Bowen. Zinc oxide and its anion: A negative ion photoelectron spectroscopic study. JOUR-NAL OF CHEMICAL PHYSICS, 109(19):8426–8429, NOV 15 1998.
- [9] LR Watson, TL Thiem, RA Dressler, RH Salter, and E Murad. High-Temperature Mass-Spectrometric Studies of the Bond-Energies of Gas-Phase ZnO, NiO, and CuO. JOURNAL OF PHYSICAL CHEMISTRY, 97(21):5577– 5580, MAY 27 1993.
- [10] CW Bauschlicher and H Partridge. A comparison of ZnO and ZnO-. JOURNAL OF CHEMICAL PHYSICS, 109(19):8430–8434, NOV 15 1998.
- [11] A.V. Gusarov and V.S. Iorish. Estimation of a priori errors in ab initio calculations of thermochemical values for the example of the dissociation energies of the zno and zns molecules. *Russian Journal of Physical Chemistry*, 80:1864– 1867, 2006.
- [12] Frederick Reif. Fundamentals of Statistical and Thermal Physics. McGraw-Hill, 1984.
- [13] R.A. Freedman H.D Young. University Physics. Addison-Wesley, 1996.
- [14] Francis W. Sears and Gerhard L. Salinger. Thermodynamics, Kinetic Theory, and Statistical Thermodynamics. Addison-Wesley, 1982.
- [15] JH Kim, X Li, LS Wang, HL de Clercq, CA Fancher, OC Thomas, and KH Bowen. Vibrationally resolved photoelectron spectroscopy of MgO- and ZnO- and the low-lying electronic states of MgO, MgO-, and ZnO. JOURNAL OF PHYSICAL CHEMISTRY A, 105(23):5709–5718, JUN 14 2001.

- [16] P.W Atkins. Physical Chemistry. Oxford, 1998.
- [17] D.R. Lide, editor. CRC Handbook of Chemistry and Physics, 73rd Edition.
   CRC Press, 1992.
- [18] Donald L. Smith. Thin-Film Deposition, Principles and Practice. McGraw-Hill, 1995.

## Chapter 5

### Nucleation of ZnO

#### 5.1 Introduction

This chapter discusses the nucleation of ZnO vapour during nanowire growth via VPT using CTR of ZnO powder. The results of the Chapter 4 indicate that while there little ZnO vapour present, it is supersaturated and would be expected to condense readily on the substrate with subsequent nanowire growth. However, little or no growth is observed experimentally, on bare substrates (i.e without buffer layers or seeds particles), indicating that there is a barrier to ZnO nucleation on such substrates. This chapter details the development of a model to calculate the amount of ZnO nucleation that takes place and compares the results to the experimental findings.

Nucleation is the process with which the formation of a new phase begins. Nuclei are formed by the aggregation of vapour molecules. The relationship between the Gibbs energy of a spherical nucleus and the nucleus size for a nucleus formed in a supersaturated vapour is shown in Figure 5.1. The Gibbs energy of the nucleus,  $\Delta G$ , increases with nucleus size until a critical size is reached, after which point the energy decreases with increasing size. If a cluster of aggregated molecules is smaller than the critical radius  $r_c$ , it will decay back into separate molecules. When the cluster size reaches a critical radius  $r_c$ , it will continue to grow. This process is illustrated in Figure 5.2.



Figure 5.1: The general form of the variation of the Gibbs energy for a spherical nucleus as a function of nucleus radius



Figure 5.2: Nuclei with  $\rm r < r_c$  will decay. Nuclei with  $\rm r > r_c$  will continue to grow

There are two types of nucleation: in the case of homogeneous nucleation the crystal nuclei form in the vapour and subsequently lands on the surface, as shown in Figure 5.3(a), while in heterogeneous nucleation molecules landing on the substrate, diffuse and nucleate to form crystals on the substrate, as illustrated in Figure 5.3(b).

The energy barrier to nucleation of ZnO nuclei is derived for both homogeneous and heterogeneous nucleation and compared to the thermal energy at that temperature. We derive a model that predicts the rates of each type of nucleation. The results show that the rates of homogeneous and heterogeneous nucleation on unseeded substrates are very small and would lead to negligible nanostructure growth. This agrees with experimental evidence which shows no nanostructure growth on bare substrates and the necessity of suitable accommodation sites or seeds for nanostructure growth to take place.



Figure 5.3: Illustration of (a) homogeneously nucleating crystals and (b) heterogeneously nucleating crystals

#### 5.2 Homogeneous nucleation of ZnO vapour

#### 5.2.1 Energy barrier to homogeneous ZnO nucleation

In the case of homogeneous nucleation, nuclei are formed in the vapour by the accumulation of vapour molecules. To calculate the nucleation barrier to homogeneous nucleation we first calculate the equilibrium critical size of the nucleating crystal. The procedure to find the energy barrier to the formation of a spherical nucleus is well established [1,2]. This analysis of nucleation barriers assumes that the nucleating crystal is a hexagonal cross section cylinder as illustrated in Figure 5.4, which is consistent with experimental reports [3]. We use the Gibbs-Curie-Wulff theorem to find the equilibrium shapes of the homogeneously nucleated crystals. The Gibbs-Curie-Wulff theorem states that, in equilibrium, the distances of the crystal faces from a point within the crystal  $(h_n)$  are proportional to the specific surface energies of these faces  $(\sigma_n)$  [1], i.e.

$$\frac{\sigma_{\rm n}}{\rm h_{\rm n}} = \rm constant \tag{5.1}$$

ZnO is an anisotropic material and thus has different values of surface energy for different faces. Recent data indicates that for the prismatic plane surface (10-10), the side faces of the crystal, the surface energy is  $\sigma_{\rm p} = 1.15 \text{ J/m}^2$ . The surface energy for the basal plane surfaces (0001), the top and bottom faces of the crystal, is  $\sigma_b = 2.0 \text{ J/m}^2$  [4].



Figure 5.4: Geometry of a homogeneously nucleated ZnO crystal

The Gibbs-Curie-Wulff theorem states:

$$\frac{\sigma_{\rm b}}{\rm b} = \frac{\sigma_{\rm p}}{\rm p} = {\rm constant}$$
 (5.2)

From geometry:

$$\mathbf{a} = \frac{2}{\sqrt{3}}\mathbf{p} \tag{5.3}$$

This gives:

b = 
$$p \frac{\sigma_b}{\sigma_p} = \frac{\sqrt{3}}{2} a \frac{\sigma_b}{\sigma_p}$$
 (5.4)

The energy of the nucleus:

$$\Delta G = \text{Surface energy term} + \text{Bulk energy term}$$
(5.5)

Surface Energy = 
$$\left(a^{2}\left[3\sqrt{3}\sigma_{b} + 6\sqrt{3}\frac{\sigma_{b}}{\sigma_{p}}\sigma_{p}\right]\right) = 9\sqrt{3}a^{2}\sigma_{b}$$
 (5.6)

Bulk Energy = 
$$-\Delta \mu \frac{V}{v_{\rm m}} = -\frac{9}{2} \frac{\Delta \mu}{v_{\rm m}} a^3 \frac{\sigma_{\rm b}}{\sigma_{\rm p}}$$
 (5.7)

$$\Delta G = 9\sqrt{3}a^2\sigma_b - \frac{9}{2}\frac{\Delta\mu}{v_m}a^3\frac{\sigma_b}{\sigma_p}$$
(5.8)

where  $\Delta \mu = \text{RT} \ln[\text{s} + 1]$  and s is the degree of supersaturation of ZnO vapour,  $\sigma_{\rm b}$  is the basal plane energy and  $\sigma_p$  is the prismatic plane energy,  $v_{\rm m}$  is the molar volume of ZnO ( $v_{\rm m} = 14.52 \times 10^{-6} \text{ m}^3/\text{mole}$  [5]). Figure 5.5 shows the variation of  $\Delta E$  with crystal side length, a at a temperature of 1200 K using the data calculated in Chapter 4 (i.e. s =  $1.99 \times 10^8$ ). The variation of the energy of the nucleus with nucleus size shown in Figure 5.5 for the values of ZnO given above reveals that the energy of the nucleus increases with increasing crystal side length, a, until it reaches a critical value where the energy begins to decrease with increasing a.



Figure 5.5: Energy of homogeneously nucleated ZnO crystal in a supersaturated vapour (s =  $1.99 \times 10^8$ ) as a function of crystal side length

Note that in Equation 5.8 the second term is negative; if the saturation is negative this function will not have a maximum. For comparison, the energy of a ZnO crystal for an undersaturated vapour (the value used is the saturation of Zn vapour of s = -0.755 found in Chapter 3 but using the facet energies of a ZnO crystal) is shown in Figure 5.6 which shows that the energy is always increasing showing that nuclei will never form in undersaturated vapour.

Maximising the energy of a homogenously formed ZnO nucleus with respect to the length of the side of the crystal a, we find the critical size of the nucleus for homogeneous nucleation. Nuclei with a side length less than  $a_c$  will spontaneously disintegrate; nuclei with a side length larger than  $a_c$  will continue to grow.



Figure 5.6: Energy of homogeneously nucleated ZnO crystal in an undersaturated vapour as a function of crystal side length

$$a_{c} = \frac{4v_{m}\sigma_{p}}{\sqrt{3}RT\ln[s+1]}$$
(5.9)

This value of  $a_c$  gives the barrier to homogeneous nucleation:

$$\Delta G_{\text{hom}} = \frac{16\sqrt{3}v_{\text{m}}^2 \sigma_{\text{p}}^2 \sigma_{\text{b}}}{\left(\text{RT}\ln\left[\text{s}+1\right]\right)^2}$$
(5.10)

At a temperature of 1200 K the energy barrier to homogeneous nucleation is 2.65 eV using the values of supersaturation calculated in Chapter 4. The energy barrier

to homogeneous nucleation shown in Figure 5.7 is more than 20 times the thermal energy at this temperature. The volume of the critical nucleus at this temperature is  $6.45 \times 10^{-29}$ m<sup>3</sup>, this corresponds to the volume of two molecules of ZnO or one unit cell of hexagonal wurtzite structure.



Figure 5.7: Energy barrier to homogeneous nucleation for ZnO nuclei as a function of temperature

#### 5.2.2 Rate of homogeneous nucleation of ZnO

The probability P, of a nuclei having enough energy to get over the energy barrier to nucleation is:

$$P = \exp\left(-\frac{\Delta G_{hom}}{k_b T}\right)$$
(5.11)

This gives an equilibrium concentration of critical nuclei, N<sup>\*</sup>:

$$N^* = N_1 \exp\left(-\frac{\Delta G_{hom}}{k_b T}\right)$$
(5.12)

where  $N_1$  is the number of molecules per unit volume

$$N_1 = \frac{p}{k_b T} \tag{5.13}$$

The classical homogeneous rate  $I_{hom}$  can be expressed in the form [1]:

$$I_{hom} = \omega^* \Gamma N^* \tag{5.14}$$

 $\omega^*$  is the frequency of the attachment of the molecules to the nucleus and is equal to the number of molecules arriving at the surface  $\times$  the surface area of the nucleus:

$$\omega^* = \frac{p}{\sqrt{2\pi m k_b T}} \times \left(3\sqrt{3} + 6\sqrt{3}\frac{\sigma_b}{\sigma_p}\right) a_c^2$$
(5.15)

where p is the partial pressure of the molecular ZnO vapour.  $\Gamma$  is known as the Zeldovich factor. The Zeldovich factor corrects (among other things) for the fact that some clusters that reach the critical size will decay to smaller sizes.

$$\Gamma = \left(\frac{\Delta G_{hom}}{3\pi n_c k_b T}\right)^{\frac{1}{2}}$$
(5.16)

where  $n_c$  is the number of molecules in the nucleus.

$$n_{c} = \frac{nucleus \quad volume}{molecular \quad volume} = \frac{9\sigma_{b}}{2\sigma_{p}} a_{c}^{2} \left(\frac{N_{A}}{v_{m}}\right)$$
(5.17)

The classical homogeneous nucleation rate  $I_{hom}(events/m^3s)$  for hexagonal particles is given by:

$$I_{\rm hom} = \left(\frac{p^2}{k_{\rm b}^2 T^2 \rho}\right) \left(\frac{2m}{\sqrt{3}\pi^2}\right)^{\frac{1}{2}} \left(3 + \frac{6\sigma_{\rm b}}{\sigma_{\rm p}}\right) \left(\frac{\sigma_{\rm p}}{\sqrt{\sigma_{\rm b}}}\right) \exp\left(-\frac{\Delta G_{\rm hom}}{k_{\rm b}T}\right)$$
(5.18)

The rate of nucleation for homogeneous are shown in Figure 5.8. The rate of homogeneous nucleation at 1200 K is  $I_{hom} = 6.58 \times 10^8$  events/m<sup>3</sup>s. In a volume of  $1 \text{ cm} \times 1 \text{ } \mu\text{m} \times 1 \text{ } \mu\text{m}$  (a surface area of  $1 \text{ } \mu\text{m}^2$  and a distance of 1 cm between source and substrate, as illustrated in Figure 5.9), over a growth time of one hour, the number of nucleation events is 0.0236. This is consistent with experimental results, which show little or no nucleation of nanowires on bare substrates.



Figure 5.8: Rate of nucleation for homogeneous nucleation of ZnO nuclei as a function of temperature



Figure 5.9: Illustration of substrate placement showing the available volume of vapour

#### 5.3 Heterogeneous nucleation of ZnO vapour

In the case of heterogeneous nucleation, nuclei form on the substrate by accumulating molecules adsorbed on the substrate.



Figure 5.10: Geometry of a heterogeneously nucleated ZnO crystal

## 5.3.1 Energy barrier to heterogeneous nucleation of ZnO without lattice mismatch

We again use the Gibbs-Curie-Wulff theorem to find the equilibrium shape of the nucleating particle, using the surface energies of ZnO as inputs, to determine the

aspect ratios of the hexagonal cylinder. The contact angle for the ZnO on the substrate is taken as  $\theta = 90^{\circ}$ , which is consistent with experimental data showing aligned ZnO hexagonal pillars grown on many substrates (with a substrate-pillar contact angle of 90°) and is a reasonable order of magnitude approximation for growth on non-wetting substrates generally.

The initial attempt to model the heterogeneous nucleation of ZnO took a similar approach to the homogeneous nucleation, except that the length of the crystal nuclei was half the length of the homogeneous nucleated crystal l = b. The energy of the nucleus:

$$\Delta G = \text{Surface energy term} + \text{Bulk energy term}$$
(5.19)

Surface Energy = 
$$\left(a^2 \left[\frac{3}{2}\sqrt{3} + 3\sqrt{3}\frac{\sigma_{\rm b}}{\sigma_{\rm p}}\right]\right)\sigma_{\rm b} = \frac{9}{2}\sqrt{3}a^2\sigma_{\rm b}$$
 (5.20)

Bulk Energy = 
$$-\Delta \mu \frac{V}{v_m} = -\frac{9}{4} \frac{\Delta \mu}{v_m} a^3 \frac{\sigma_b}{\sigma_p}$$
 (5.21)

$$\Delta G = \frac{9}{2}\sqrt{3}a^2\sigma_b - \frac{9}{4}\frac{\Delta\mu}{v_m}a^3\frac{\sigma_b}{\sigma_p}$$
(5.22)

This value gives a barrier to heterogeneous nucleation of:

$$\Delta G_{het} = \frac{8\sqrt{3}v_m^2 \sigma_p^2 \sigma_b}{\left(RT \ln [s+1]\right)^2}$$
(5.23)

This gives a value for the energy barrier smaller than the barrier to homogeneous

nucleation, as shown in Figure 5.11. This result suggests that the amount of heterogeneous nucleation is substantial,  $3 \times 10^{12}$  events/µm<sup>2</sup> in one hour, which is inconsistent with experimental evidence that indicates little or no nucleation. However, we note here that the energy barrier here is the energy barrier to the formation of ZnO nuclei on a lattice matched substrate, such as the ZnO buffer layer. ZnO nanowire growth is observed on the ZnO buffer layer deposited portions of the substrate agreeing with the finding that nucleation on a lattice matched substrate takes place readily. To calculate an exact value for the nucleation of ZnO nuclei on the ZnO buffer layer, the textured nature of the substrate needs to also be considered but this provides a first step in examining the process.



Figure 5.11: Energy barrier to heterogeneous nucleation of ZnO nuclei as a function of temperature without lattice mismatch

## 5.3.2 Energy barrier to heterogeneous nucleation of ZnO including lattice mismatch

The previous approach ignores the effect of the substrate on the nucleus. There is a lattice mismatch between ZnO and Si. ZnO growing on a silicon substrate would therefore be subjected to strain as the crystal attempts to match up with the substrate spacing, as illustrated in Figure 5.12.



Figure 5.12: Illustration of the lattice mismatch between ZnO and Si

An additional term to estimate for the strain due to the lattice mismatch between the substrate and ZnO is added [6]. The lattice mismatch  $\epsilon$  is given by:

$$\epsilon = \frac{\mathbf{a}_{\mathrm{Si}} - a_{\mathrm{ZnO}}}{\mathbf{a}_{\mathrm{Si}}} = 0.4 \tag{5.24}$$

The energy

$$\Delta G = \text{Surface energy term} + \text{Bulk energy term} + \text{Strain term}$$
(5.25)

Strain Energy = 
$$\frac{1}{2} Y \epsilon^2 \times Volume = \frac{1}{2} Y \epsilon^2 \left(\frac{9}{4} a^3 \frac{\sigma_b}{\sigma_p}\right)$$
 (5.26)

where Y is the Young's modulus of ZnO (estimated to be 100 GPa [7]). In reality, the lattice mismatch  $\epsilon$  would be larger than the value 0.4 calculated using the lattice parameters of Si, because the substrate will be silicon with a thin layer of silicon dioxide. The lattice mismatch between ZnO and SiO<sub>2</sub> will be ~ 0.6 [8–10]. This would lead to a much greater energy barrier and a much lower rate of nucleation. We take the calculation for Si as a maximum possible number of nucleation events, but in an experimental situation the number would be smaller, due to the presence of the layer of SiO<sub>2</sub>, which is always present on a Si surface in an environment containing oxygen.

$$\Delta G = \frac{9\sqrt{3}}{2}a^2\sigma_b - \frac{\Delta\mu}{v_m}\frac{9}{4}a^3\frac{\sigma_b}{\sigma_p} + \frac{1}{2}Y\epsilon^2\left(\frac{9}{4}a^3\frac{\sigma_b}{\sigma_p}\right)$$
(5.27)

The variation of the energy of the nucleus with nucleus size is shown in Figure 5.13. Maximising this energy with respect to the length of the side of the crystal a, finds the critical size of the nucleus for heterogeneous nucleation.

$$a_{c} = \frac{4}{\sqrt{3}} \frac{2v_{m}}{2RT\ln[s+1] - v_{m}Y\epsilon^{2}}\sigma_{p}$$

$$(5.28)$$



Figure 5.13: Energy of heterogeneously nucleated ZnO crystal as a function of crystal side length



Figure 5.14: Energy barrier to heterogeneous nucleation of ZnO as a function of temperature

The energy barrier  $\Delta E_{het}$  to heterogeneous 3D nucleation for such a nucleus is:

$$\Delta G_{het} = 8\sqrt{3}\sigma_p^2 \sigma_b \left(\frac{2v_m}{2RT\ln[s+1] - v_m Y\epsilon^2}\right)^2$$
(5.29)

The energy barrier to heterogeneous nucleation is shown in Figure 5.14 and at 1200 K is 8.63 eV. This is a large value compared to the thermal energy at this temperature, due to the large lattice mismatch between the ZnO and Si/SiO<sub>2</sub> substrate, which leads to a large strain term in the energy barrier to nuclei formation.

#### 5.3.3 Rate of heterogeneous nucleation of ZnO

In a similar expression to the rate for homogeneous nucleation, the rate of heterogeneous nucleation is given by:

$$I_{het} = \omega^* \Gamma N_0 \exp\left(-\frac{\Delta G_{het}}{k_b T}\right)$$
(5.30)

however, in this case we refer to the number of nuclei forming on the substrate so  $N_0$  is the number of adsorption sites  $(1 \times 10^{15} \text{ cm}^{-2} \text{ [2]})$  as opposed to the number of molecules per volume. The rate of arrival of molecules to the nucleus is  $\omega^*$ ,  $\Gamma$  is the Zeldovich factor. The molecules can arrive at the nucleus in two different ways, as illustrated in Figure 5.15. Molecules adsorbed on the substrate can diffuse to the perimeter of the nucleus. In addition, molecules can condense directly from the vapour on to the nucleating crystal.



Figure 5.15: (a)View from above of adsorbed molecules on the substrate arriving at the perimeter of the crystal (b) Molecules arriving at the crystal surface area from vapour

We first find the rate of arrival of diffusing adsorbed molecules to the perimeter of the crystal in the two dimensional case:

$$\omega_{\rm a} = J_{\rm s} \times \text{Perimeter length} \tag{5.31}$$

where  $J_s$  is the number of molecules arriving per second per meter on the substrate at the nucleus perimeter and is given by:

$$J_{s} = D_{s} \nabla n_{s} \approx D_{s} \frac{n_{s}}{a_{d}}$$
(5.32)

 $D_s$  is the diffusion coefficient of the molecules on the substrate,  $n_s$  is the number density of molecules on the substrate and  $a_d$  is the length of a diffusion jump. The number density of molecules on the substrate is the number arriving on the substrate  $\times$  the mean time of molecules remaining adsorbed on the substrate ( $\tau$ ).

$$n_{\rm s} = \frac{p\tau}{\sqrt{2\pi m k_{\rm b} T}} \tag{5.33}$$

The diffusion length of the molecules is  $\lambda = \sqrt{2D_s\tau}$  which gives:

$$J_{s} = \frac{p}{\sqrt{2\pi m k_{b} T}} \left(\frac{4\lambda^{2}}{a_{d}}\right)$$
(5.34)

The perimeter of the nucleus is  $6a_c$ . The rate of arrival of adsorbed molecules on the substrate to the nuclei is given by:

$$\omega_{\rm a} = 8\sqrt{3} \frac{\mathrm{p}\sigma_{\rm p}}{\sqrt{2\pi\mathrm{m}k_{\rm b}T}} \left(\frac{2\mathrm{v}_{\rm m}}{2\Delta\mu - 2\mathrm{v}_{\rm m}\mathrm{Y}\epsilon^2}\right) \left(\frac{4\lambda^2}{\mathrm{a}_{\rm d}}\right)$$
(5.35)

The rate of arrival of molecules from the vapour is given by the number of molecules arriving at the surface  $\times$  the surface area of the nucleus:

$$\omega_{\rm b} = \frac{\rm p}{\sqrt{2\pi \rm mk_b T}} \times \left(\frac{3}{2}\sqrt{3} + 3\sqrt{3}\frac{\sigma_{\rm b}}{\sigma_{\rm p}}\right) a_{\rm c}^2 \tag{5.36}$$

Figure 5.16 shows that the number of molecules arriving onto the substrate and diffusing to the nucleating crystal is far greater than the number of molecules arriving from the vapour. We will now include only the contribution of molecules diffusing to the crystal on the substrate *i.e*  $\omega^* = \omega_a$ .



Figure 5.16: Rate of arrival of molecules ( $\omega_a$  (solid line),  $\omega_b$  (dashed line)) to the nucleating crystal as a function of temperature

 $\Gamma$ , the Zeldovich factor is given by:

$$\Gamma = \left(\frac{\Delta G_{het}}{3\pi n^* k_b T}\right)^{\frac{1}{2}}$$
(5.37)

$$\Gamma = \frac{1}{\sqrt{3\pi k_{\rm b}T}} \left( \frac{\sqrt{8\sqrt{3}v_{\rm m}}}{16\sqrt{3}N_{\rm A}\sigma_{\rm p}\sqrt{\sigma_{\rm b}}} \right) \left( \frac{2\Delta\mu - Y\epsilon^2 v_{\rm m}}{2v_{\rm m}} \right)^2$$
(5.38)

The nucleation rate for heterogeneously nucleating particles is found to be:

$$I_{het} = \frac{v_m N_o}{N_A \sqrt{\sigma_b \sqrt{3}}} \left(\frac{p}{\pi m k_b T}\right) \left(\frac{2RT \ln[s+1] - v_m Y \epsilon^2}{2v_m}\right) \frac{4\lambda_d^2}{a_d} \exp\left(-\frac{\Delta G_{het}}{k_b T}\right)$$
(5.39)

where  $\lambda_d$  is the estimated diffusion length of ZnO on silicon (here estimated to be

1  $\mu$ m based on species diffusion lengths deduced for nanowire growth in other binary compound materials at about 1200 K [11]). The hopping distance is approximated as  $a_d = 0.3$  nm [2].



Figure 5.17: Rate of nucleation for heterogeneous nucleation of ZnO nuclei as a function of temperature

The rate of heterogeneous nucleation for ZnO is shown in Figure 5.17. On a Si/SiO<sub>2</sub> substrate at 1200 K is  $I_{het} = 2.57 \times 10^{-9}$  events/m<sup>2</sup>s. In an area of 1 µm × 1 µm, over a growth time of one hour, the number of events is  $9.25 \times 10^{-18}$ . This is a negligible number of nucleation events and is consistent with the experimental results, showing no growth on such a bare Si/SiO<sub>2</sub> substrate.

#### 5.4 Conclusions

This chapter discusses the nucleation of ZnO during VPT growth. It describes the development of a model to calculate the energy barriers to both homogeneous and heterogeneous nucleation and the rate of nucleation of ZnO.

The barrier to homogeneous nucleation of ZnO vapour is 2.65 eV. The number of nucleation events in one hour, in a volume of  $1 \text{ cm} \times 1 \mu \text{m} \times 1 \mu \text{m}$ , is 0.024 events. The number of nucleation events is small but not completely negligible; it is conceivable that some nuclei might form homogeneously and land on the substrate surface, for example we note occasional growth of ZnO nanostructures on unseeded areas of substrate. We also note that during growth, the native silicon dioxide tends to grow around and consume surface particulates, which also mitigates against substantial ZnO growth on these nuclei [3].

The barrier to heterogeneous nucleation of ZnO vapour, when the lattice mismatch between the nucleating crystal and the substrate is taken into account, is found to be 8.63eV. This is larger than the barrier to homogeneous nucleation. The rate of heterogeneous nucleation events over a growth time of one hour and in an area of 1  $\mu$ m × 1  $\mu$ m is 9.25 × 10<sup>-18</sup> events; this is negligible.

These results agree with experiments that show no ZnO nanostructure growth on bare substrates. For growth to occur, seeds or nucleation sites are required, where the barriers to nucleation are overcome.

## Bibliography

- I.V Markov. Crystal Growth for Beginners, 2nd edition. World Scientific, London, 2003.
- [2] Donald L. Smith. Thin-Film Deposition, Principles and Practice. McGraw-Hill, 1995.
- [3] Daragh Byrne, Rabie Fath Allah, Teresa Ben, David Gonzalez Robledo, Brendan Twamley, Martin O. Henry, and Enda McGlynn. Study of Morphological and Related Properties of Aligned Zinc Oxide Nanorods Grown by Vapor Phase Transport on Chemical Bath Deposited Buffer Layers. CRYSTAL GROWTH & DESIGN, 11(12):5378–5386, DEC 2011.
- [4] A. Wander, F. Schedin, P. Steadman, A. Norris, R. McGrath, T. S. Turner,
   G. Thornton, and N. M. Harrison. Stability of polar oxide surfaces. *Phys. Rev. Lett.*, 86(17):3811–3814, Apr 2001.
- [5] D.R. Lide, editor. CRC Handbook of Chemistry and Physics, 73rd Edition. CRC Press, 1992.
- [6] BW Wessels. Morphological stability of strained-layer semiconductors. JOUR-NAL OF VACUUM SCIENCE & TECHNOLOGY B, 15(4):1056–1058, JUL-AUG 1997.

- [7] G. Stan, C. V. Ciobanu, P. M. Parthangal, and R. F. Cook. Diameter-dependent radial and tangential elastic moduli of ZnO nanowires. NANO LETTERS, 7(12):3691–3697, DEC 2007.
- [8] Dukhyun Choi Kihong Kim Hyeon-Jin Shin Seon-Mi Yoon Jae-Young Choi Sang-Woo Kim Won Mook Choi, Kyung-Sik Shin. Selective growth of zno nanorods on sio2/si substrates using a graphene buffer layer. Nano Research, 4(5):440-447, 2011.
- KO Ng and D Vanderbilt. Structure and oxidation kinetics of the Si(100)-SiO2 interface. *PHYSICAL REVIEW B*, 59(15):10132–10137, APR 15 1999.
- [10] N. Shi and R. Ramprasad. Atomic-scale dielectric permittivity profiles in slabs and multilayers. *PHYSICAL REVIEW B*, 74(4), JUL 2006.
- [11] Shadi A. Dayeh, Edward T. Yu, and Deli Wang. Surface Diffusion and Substrate-Nanowire Adatom Exchange in InAs Nanowire Growth. NANO LET-TERS, 9(5):1967–1972, MAY 2009.

## Chapter 6

## Relationship between the length and radii of ZnO nanowires

#### 6.1 Introduction

This chapter examines the final stage of the VPT growth of ZnO nanowires. In this stage molecules are incorporated into the already growing nanowires. We describe a model to calculate the growth rate of ZnO nanowires, allowing us to study the relationship between the length and radius of a ZnO nanowire.

The dimensions of a nanowire are relevant to many practical application of ZnO nanowires, such as lasing threshold [1], gas sensing applications [2] and voltagecurrent characteristics [3]. The relationship between the length and radius of a nanowire also gives us information about the growth mechanism of the nanowire.

The growth rate and final length of crystal whiskers has been the subject of many studies. The first observation of whisker growth from the vapour phase was by Sears, who proposed a growth mechanism for mercury whiskers [4]. Sears calculated a growth rate based on the hypothesis that only atoms striking the top of the

#### 6.1 Introduction

whisker contributed to growth. Sears recognised that the discrepancy between the measured and calculated rates showed that atoms striking the whisker elsewhere and diffusing to the top also contributed to the growth. In a study of the field emission of mercury whiskers, Gomer [5] reported an initial exponential growth law for whiskers, confirming that whisker growth occurs by diffusion of impinging molecules to the whisker end. Ruth and Pound [6] and Blakeley and Jackson [7] explored the problem of surface diffusion-controlled whisker growth further. The diffusion theory discussed in these studies gives a model that gave an exponential growth law for lengths less than the diffusion length  $\lambda$ , and a linear law for lengths greater than  $\lambda$ . Parker *et al.* [8] verified this linear law by examining the length rates as a function of time of growth. These diffusion-based models predict that the growth rate and length of a whisker are inversely proportional to the radius of the whisker.

Givargizov [9], discussing VLS growth, found that the growth rate and final length of Si whiskers grown in the  $SiCl_4/H_2$  system were directly proportional to the whisker diameter. This can be attributed to the role of the Gibbs-Thomson effect, which elevates the adatom chemical potential in the alloy droplet in a VLS growth.

Recently there has been renewed interest in the application of the diffusion theory to the growth mechanism and growth rate of nanowires. Schubert *et al.* [10] examined the radius dependence of the growth rate of Si nanowhiskers grown by MBE on Au, deposited on Si substrates, and observed an opposite relationship to Givargizov. Johansson *et al.* [11] also observed an inverse relationship between nanowire length and radius for GaP nanowires grown by MOVPE on Au particles. This paper derived a model to calculate the length rate of nanowires, including the diffusion of molecules from the nanowire sidewalls and the substrate, and addressed the Gibbs-Thomson effect showing that this is only relevant at small supersaturations, such as those in Givargizov's experiments. Dubrovskii *et al.* [12] measured the inverse dependence of GaAs nanowires grown by MBE on GaAs substrates using Au as a catalyst for VLS growth.

Diffusion-induced growth has also been applied to ZnO nanowires. Kim *et al.* [13] examined the growth mechanism of ZnO nanowires grown using CTR via VPT on small Au clusters. They measured an inversely proportional relationship between the length and diameter of these nanowires. They did not attempt to calculate an exact value for the growth rate but noted that the measured values for the lengths are given by  $L \approx 1/d + c$ , where c is a constant value and d is the nanowire diameter. Oh *et al.* [14] studied ZnO and In-doped ZnO nanowires grown via VPT, using Zn powder as a source, on both AuGe and Ti deposited Si substrates. This paper applied a model for VLS growth to the measured values, although the nanowires did not show evidence of a VLS growth mechanism, and found an inversely proportional relationship between the length and radius of nanowires. Hejazi and Hosseini have presented a diffusion-controlled kinetic model for Au-catalyzed ZnO growth that also predicts a growth rate that is inversely dependent to the radius [15].

## 6.2 Model to calculate the length of a nanowire as a function of nanowire radius

This model follows the model for mass transport model derived for metal-particle assisted growth of III/IV nanowires developed by J. Johansson [11]. Slight amendments to the existing model were made to take account of the slightly different morphology observed in our grown nanowires, with flat top surfaces, compared to those with rounded top surfaces considered in the original model. Specifically, the model is altered for application to VS growth of ZnO nanowires on a ZnO buffer layer by considering a circular collection area for atoms/molecules on the top of the nanowire as opposed to a hemispherical collection area.

Growth is assumed in this model to only take place only at the top of the nanowire; the radius is assumed to be constant throughout. ZnO is an anisotropic material, with different values of surface energy for different faces which leads to preferential growth along the c-axis. The top of the nanowire, the (0001) basal plane surface, is a polar face that is Zn or O terminated whereas the side faces of the nanowire are non polar. Although atom/molecule incorporation on the sides of the nanowire is possible, here we consider the ideal case where incorporation only takes place on the top of the nanowire. Atoms/molecules can arrive from the vapour to the top of a growing nanowire in three ways.

- 1: Atoms/molecules arrive directly on the top of the growing nanowire.
- Atoms/molecules impinge on the sidewalls of the growing nanowire and diffuse to the top.
- 3: Atoms/molecules impinge onto the substrate, diffuse to the nanowire and then up the sidewall to the top.

We will look at each of the contributing terms separately.



Figure 6.1: Illustration of the impingement of molecules on a growing nanowire

## 6.2.1 Term 1: Atoms/molecules arriving directly to the top of the nanowire

The rate at which the length of a nanowire increases, as a result of molecules arriving at the top of the nanowire, is given by the impingement rate (the number of molecules per unit area per second)  $\times$  the molecular volume of the molecules incorporated into the nanowire. Here we take the collection area to be a flat circle as opposed to the hemispherical collection area by Johansson [11].

$$\frac{\partial L}{\partial t} = \Omega J_t \tag{6.1}$$

Where L is the length of the nanowire,  $\Omega$  is the molecular volume and  $J_t$  is the impingement rate of the molecules from the vapour on to the top of the nanowire

and is given by the Knudsen equation [16]:

$$J_{t} = \frac{p}{\sqrt{2\pi m k_{b} T}}$$
(6.2)



Figure 6.2: Schematic of growing nanowire

# 6.2.2 Term 3: Atoms/molecules diffusing from the substrate to the top of the nanowire

We examine term 3 before term 2 (as defined in Section 6.2) as the molecules from the substrate will join the molecules on the sidewire. The net flux of atoms/molecules arriving on the substrate is given by:

$$J_{s} - \frac{n_{s}}{\tau_{s}}$$
(6.3)
where  $J_s$  is the impingement rate of molecules onto the substrate,  $\tau_s$  is the mean lifetime of the molecule on the substrate and  $n_s$  is the surface density of molecules on the substrate. On the substrate surface, the number density of molecules on the substrate surface is described by:

$$D_s \bigtriangledown^2 n_s - \frac{n_s}{\tau_s} + J_s = \frac{\partial n_s}{\partial t}$$
 (6.4)

Where the Laplacian in polar coordinates is  $\nabla^2 = \frac{\partial^2}{\partial r^2} + 1/r\frac{\partial}{\partial r}$  and  $D_s$  is the diffusion constant for molecules on the substrate. The diffusion length of molecules on the substrate  $\lambda_s$  is given by:

$$\lambda_s = \sqrt{\mathbf{D}_{\mathbf{s}} \tau_{\mathbf{s}}} \tag{6.5}$$

We examine the steady state case, i.e.  $\frac{\partial n_s}{\partial t} = 0$ . Once a molecule reaches the base of the nanowire it becomes a molecule on the wire and is no longer counted as a mobile molecule on the substrate; see Figure 6.2 for a schematic diagram explaining the coordinates used, so that,

$$\mathbf{n}_s \left( \mathbf{r} = \mathbf{r}_{\mathbf{w}} \right) = 0 \tag{6.6}$$

The solution to Equation 6.4 with this boundary condition, contains modified Bessel functions of the second order,  $K_0$  [17].

$$n_{s}(r) = J_{s}\tau_{s} \left[ 1 - \frac{K_{0}(\frac{r}{\lambda_{s}})}{K_{0}(\frac{r_{w}}{\lambda_{s}})} \right]$$
(6.7)

#### 6.2 Model to calculate the length of a nanowire as a function of nanowire radius

Figure 6.3 shows the value of  $\left[1 - \frac{K_0(\frac{r}{\lambda_s})}{K_0(\frac{r_w}{\lambda_s})}\right]$  as a function of the distance from the nanowire, r. The atom/molecule density will reach the constant value of  $J_s\tau_s$  for large distances from the nanowire base, for this to occur we need a large interwire separation, which needs to be larger than the species diffusion length, or the value of the flux from the substrate will be smaller.

This gives a flux from the substrate to the nanowire:

$$J_{sw} = D_w \left. \frac{\partial n_w}{\partial z} \right|_{z=0} = -J_s \lambda_s \frac{K_1(\frac{r_w}{\lambda_s})}{K_0(\frac{r_w}{\lambda_s})}$$
(6.8)



Figure 6.3: Atom/molecule density on the substrate as a function of distance from the nanowire

## 6.2.3 Term 2: Atoms/molecules diffusing from the sidewalls to the top of the nanowire

The net flux of molecules arriving at the sidewall from the vapour is given by:

$$J_{w} - \frac{n_{w}}{\tau_{w}} \tag{6.9}$$

Where  $J_w$  is the impingement rate of molecules onto the side of the nanowire,  $\tau_w$  is the mean lifetime of the molecule on the sidewall and  $n_w$  is the density of molecules on the sidewall. We can describe the density of molecules on the sidewall,  $n_w$  by the one dimensional diffusion equation:

$$D_{w}\frac{\partial^{2}n_{w}}{\partial z^{2}} + J_{w} - \frac{n_{w}}{\tau_{w}} = \frac{\partial n_{w}}{\partial t}$$
(6.10)

Again, we consider the steady state case where  $\frac{\partial n_w}{\partial t} = 0$ .

A typical trial solution to a partial differential equation of the form of Equation 6.10 is [17]:

$$n_w(z) = aCosh\left(\frac{z}{\lambda_w}\right) + bSinh\left(\frac{z}{\lambda_w}\right) + c$$
 (6.11)

The boundary conditions are:

• The density of molecules at the top of the wire must be zero. Once molecules arrive at the top of the wire they are incorporated into the wire, they are no longer mobile molecules on the sidewall, see Figure 6.2 for a schematic diagram explaining

the coordinates used..

$$n_w(z = L) = 0$$
 (6.12)

• The flux of molecules from the substrate to the wire must equal the flux of molecules from the wire to the substrate.

$$D_{w} \left. \frac{\partial n_{w}}{\partial z} \right|_{z=0} = -D_{s} \left. \frac{\partial n_{s}}{\partial r} \right|_{r=r_{w}}$$
(6.13)

Substituting the trial solution into Equation 6.10 gives  $c = J_w \tau_w$ . Using the boundary condition Equation 6.12 we find that

$$a = \frac{-J_{w}\tau_{w} - bSinh\left(\frac{z}{\lambda_{w}}\right)}{Cosh\left(\frac{z}{\lambda_{w}}\right)}$$
(6.14)

The boundary condition Equation 6.13 and Equation 6.7 gives:

$$\mathbf{b} = \frac{\mathbf{j}_{sw}}{\lambda_w \mathbf{D}_{w}} \tag{6.15}$$

where

$$j_{sw} = -J_s \lambda_s \frac{K_1(\frac{r_w}{\lambda_s})}{K_0(\frac{r_w}{\lambda_s})}$$
(6.16)

Substituting a, b and c into Equation 6.11 gives the density of molecules on the sidewall of the nanowire:

$$n_{w} = J_{w}\tau_{w} \left[ 1 - \frac{\operatorname{Cosh}(\frac{z}{\lambda_{w}})}{\operatorname{Cosh}(\frac{L}{\lambda_{w}})} \right] - \frac{j_{sw}\lambda_{w}}{D_{w}} \frac{\operatorname{Sinh}(\frac{L-z}{\lambda_{w}})}{\operatorname{Cosh}(\frac{L}{\lambda_{w}})}$$
(6.17)

This gives a contribution of molecules from the sidewalls and the substrate to the length rate of:

$$\frac{\partial \mathbf{L}}{\partial \mathbf{t}} = -\mathbf{D}_{\mathbf{w}} \left. \frac{\partial \mathbf{n}_{\mathbf{w}}}{\partial \mathbf{z}} \right|_{\mathbf{z}=L} \times 2\frac{\Omega}{\mathbf{r}_{\mathbf{w}}} \tag{6.18}$$

The total growth rate of ZnO nanowires is:

$$\frac{\partial \mathcal{L}}{\partial t} = \frac{2\Omega J \lambda_w}{r_w} \operatorname{Tanh}\left(\frac{\mathcal{L}}{\lambda_w}\right) - \frac{2\Omega j_{sw}}{r_w \operatorname{Cosh}(\frac{\mathcal{L}}{\lambda_w})} + \Omega J$$
(6.19)

where

$$j_{sw} = -J_s \lambda_s \frac{K_1(\frac{r_w}{\lambda_s})}{K_0(\frac{r_w}{\lambda_s})}$$
(6.20)

Equation 6.19, when  $L >> \lambda_w$ , reduces to:

$$\frac{\partial \mathcal{L}}{\partial t} = \mathcal{J}\left(1 + 2\frac{\lambda_{w}}{r_{w}}\right) \tag{6.21}$$

#### 6.2.4 Model results

We integrate the growth rate found using Equation 6.19 from zero to the growth time to give the length of the nanowire. These calculations are performed using MATLAB. There are no reported values for the diffusion length of Zn atoms on the sidewalls of ZnO nanowires or on the ZnO buffer layer substrate. We estimate these to fit the data,  $\lambda_s = \lambda_w = 100$ nm. These values are of a comparable order of magnitude to other findings for ZnO and similar molecules [11, 14, 18]. In their study of ZnO nanowires, Oh *et al.* [14] found a best fit using a diffusion length of 180 nm for Zn adatoms on ZnO nanowire sidewalls. Johnasson *et al.* [11] found a diffusion length for Ga on GaP nanowire sidewalls of ~ 350 nm gave the best fit between experimental results and theory. In a study of the diameter dependent growth rate of InAs nanowires, Froberg *et al.* [18] found a value of 130 nm for the diffusion length of In atoms on InAs gave the best results for comparison to experimental results.

The impingement rate, estimated from the number of molecules necessary to have the density of nanowires observed in Section 6.3.1, is  $J = 0.85 \times 10^{19}$  molecules/m<sup>2</sup>s. The growth duration is taken to be 30 minutes.

The growth rate of a nanowire as a function of growth time for a nanowire of radius 100 nm is shown in Figure 6.4. The growth rate initially increases with time, since the molecule contribution from the sidewalls will increase as the nanowire lengthens. As the nanowire grows and  $L > \lambda$ , the contribution of molecules from the substrate decreases. Eventually when  $L >> \lambda_w$ , the growth rate decreases to the constant value predicted by Equation 6.21.



Figure 6.4: Nanowire growth rate as a function of time

Figure 6.5 shows the the nanowire length as a function of time, comparing the nanowire length found using two models: the first only including atoms/molecules from direct impingement on the top of the nanowire and atoms/molecules diffusing from the sidewalls (term 1 + 2), the second, a model that also includes molecules diffusing from the substrate (term 1 + 2 + 3). After ~ 600 s there is no difference between the results of the two models. The contribution of molecules diffusing from the substrate decreases as the length of the nanowire increases beyond the molecular diffusion length.



Figure 6.5: Nanowire length as a function of time showing effect of different terms

Figure 6.6 shows the length of the nanowires as a function of radius for a growth duration of 30 minutes. The length of the nanowire calculated using a model that includes only molecules impinging on the top of the nanowire (term 1) is shown. These lengths are constant for all nanowire radii. Figure 6.6 also shows the length when molecules diffusing from the sidewall (term 1 + 2) and molecules from the sidewall and substrate (terms 1 + 2 + 3) are included in the model. There is no difference between these curves. After 30 minutes the molecules from the substrate no longer reach the top of the nanowire, so including this term does not affect the final length. The lengths shown in Figure 6.6 decrease with increasing radius.



Figure 6.6: Nanowire length as a function of radius

#### 6.3 Comparison of model to experimental results

This section compares the results of experimental growth measurements to those predicted by model derives and described above. There are three possible general outcomes of these measurements:

1. All of the nanowires are the same length regardless of nanowire radius. This would suggest that only molecules impinging on the top of the nanowire contribute to nanowire growth.

2. The length of the nanowires increases with decreasing radius, i.e. thinner nanowires are longer than thicker ones. This supports the need for inclusion of terms to account for molecules diffusing from the sidewalls of the nanowires to the top. 3. The length of the nanowires increases with increasing radius. This would indicate another physical effect, not considered in our analysis, at work during the growth.

We cannot examine in detail the relationship between the length and the growth time of a nanowire, since we can only estimate the growth duration, and do not have the fine control over the growth duration that is required to measure the initial growth rate. To study the initial growth rate we would need to look at nanowires grown for periods less than 600 s. To have fine control over the growth time, control over the availability of source materials is necessary. The furnace takes between 10-15 minutes to reach the growth temperature and requires 3-4 hours to cool down to room temperature making the actual time that source material is present at a set temperature a broader estimate than would be needed to explore the variation in growth rate for short times.

#### 6.3.1 ZnO nanowires grown via VPT

Figure 6.7 shows the results of a VPT growth at a temperature of 1200 K. This figure shows clearly that ZnO nanowires with different radii are of different lengths. The radii are thought to be determined by the underlying ZnO buffer layers, specifically the dimensions of the ZnO nanorods deposited by CBD. The measurements of these lengths and radii are shown in Figure 6.8. The length as a function of radius found using the model is also shown. This VPT growth method makes use of the residual  $O_2$  present in the furnace after a 10-15 minute flushing period, the exact number of molecules arriving at the sample substrate is unknown. We are unable to calculate an exact impingement rate for Zn or  $O_2$  molecules as we do not have a value for the partial pressure of the  $O_2$  present in the furnace. The impingement



Figure 6.7: SEM images of ZnO nanowires grown via general VPT

rate is estimated from the number of molecules necessary to have a density of ~ 40 nanowires/ $\mu$ m<sup>2</sup> of length 2  $\mu$ m and diameter 75 nm over the growth time to be  $J = 0.85 \times 10^{19}$ molecules/m<sup>2</sup>s. As has been discussed in previous chapters, there will also be a smaller amount ZnO molecules impinging on the nanowire. For simplicity we just deal with the larger value of Zn atoms arriving. The growth time used was 30 minutes as measured for general VPT growth in Chapter 2. Figure 6.7 shows that the interwire separation is not larger than the estimated diffusion length 100 nm. This is not a large concern because as has been shown above, the effect of the atom/molecule contribution from the substrate is not expected to have a major effect on the overall length of the nanowires.

The length and radii measurements have a significant degree of scatter but certainly do show a general trend of increasing length with decreasing radius. The model parameters can be varied to show general good agreement with the experimental results, but without a reasonable estimate of the number of molecules it is difficult to claim very good agreement with the model, beyond the reduction of nanowire length with increasing radius. This observed relationship does however strongly support the inclusion of molecules diffusing from the sidewalls of the nanowire.



Figure 6.8: Nanowire length as a function of radius for sample with a growth time of 30 minutes

## **6.3.2** ZnO nanowires grown in 2.0 sccm of $O_2$

The nanowires discussed in this section were grown in a specific amount of  $O_2$  for 40 minutes at a temperature 1200 K. This allows the calculation of an exact value for the number of impinging molecules,  $J=\alpha J_{O_2}$ , where  $\alpha$  is the sticking coefficient of  $O_2$  as calculated in Chapter 3. The measured value of introduced  $O_2$  is 2.0 sccm, which gives a molecule arrival rate of  $\alpha J_{O_2}=2.65 \times 10^{19}$  molecules/m<sup>2</sup>s. As shown in Figure 6.9, the sample grown in an introduced amount of  $O_2$  shows a much denser coverage than samples grown in a VPT growth that makes use of the residual  $O_2$  present in the furnace.

Figure 6.10 shows the measurements of the lengths and radii of ZnO nanowires grown for a duration of 40 minutes. This figure also shows the calculated lengths



Figure 6.9: SEM images of ZnO nanowires grown in 2.0 sccm of  $O_2$  for 40 minutes

for a growth duration of 40 minutes and for an impingement rate of  $J=\alpha J_{O_2}$  and  $J=0.75\alpha J_{O_2}$ . The factor of 0.75 is included to provide a better fit to the data but a range of values would provide a good fit. The measurements show again an overall decrease in nanowire length with an increase in nanowire radius. The values for lengths found for  $J=0.75\alpha J_{O_2}$  are in good agreement with the measured values.



Figure 6.10: Nanowire length as a function of radius for sample grown for 40 minutes in 2.0 sccm of  $O_2$ 

Figure 6.11 shows nanowires that were grown for 20 minutes in a specific amount of O<sub>2</sub>. These nanowires are, as expected, shorter overall than those grown for a duration of 40 minutes. The calculated lengths for a duration of 20 minutes are compared to the measured values in Figure 6.12. Again the measured values show better agreement with the model using a molecule impingement rate  $J=0.75\alpha J_{O_2}$ .



Figure 6.11: SEM images of ZnO nanowires grown in 2.0 sccm of  $O_2$  for 20 minutes



Figure 6.12: Nanowire length as a function of radius for sample grown for 20 minutes in 2.0 sccm of  $O_2$ 

#### 6.4 Conclusions

This chapter describes the physical basis, derivation and application of a model to calculate the growth rate of ZnO nanowires. The model includes contributions of molecules from direct impingement onto the top of the nanowire and molecules diffusing from the sidewalls and from the substrate.

Calculations of the growth rate of a nanowire show that the inclusion of molecules diffusing from the substrate to the top of the nanowire is only relevant during the initial stages of growth. The nanowire growth rate decays to a constant value once the nanowire has reached a length greater than the diffusion length of the molecules on the sidewall of the nanowire. The model shows that when molecules impinging directly onto the nanowire top are considered alone, the predicted length of the nanowire is identical regardless of the nanowire radius. When molecules diffusing from the side walls are included in the model, the calculated length of the nanowire decreases with increasing radius.

Measured values of the length and radius of nanowires grown via VPT on ZnO buffer layers show that thinner nanowires are longer than thicker nanowires, supporting the inclusion of molecules diffusing from the sidewalls in the model. For growths using the residual  $O_2$  in the furnace, it is impossible to accurately compare the predicted values with the actual measured values, as both the impingement rate of molecules and the diffusion lengths of the molecules are unknown.

When growths are performed in a specific amount of  $O_2$ , the impingement rate can be calculated. The best agreement is found for an impingement rate that is 75% the exact calculated value. This is a reasonable estimate for the number of molecules arriving at the substrate. The lengths calculated for two different growth times agree with the measured values showing reasonable agreement for the predicted variation of nanowire lengths with time.

Overall the experimental results support the inclusion of molecules diffusing from the sidewalls in a model to calculate the growth rate and radius dependency of the length of ZnO nanowires grown via VPT.

## Bibliography

- A. N. Gruzintsev, G. A. Emelchenko, A. N. Red'kin, W. T. Volkov, E. E. Yakimov, and G. Visimberga. The dependence of the lasing threshold in ZnO nanorods on their length. *SEMICONDUCTORS*, 44(9):1217–1221, SEP 2010.
- [2] Michelle J. S. Spencer. Gas sensing applications of 1D-nanostructured zinc oxide: Insights from density functional theory calculations. *PROGRESS IN MATERIALS SCIENCE*, 57(3):437–486, APR 2012.
- [3] Zhiwen Yang, Bin Wen, Roderick Melnik, Shan Yao, and Tingju Li. Geometry dependent current-voltage characteristics of ZnO nanostructures: A combined nonequilibrium Green's function and density functional theory study. AP-PLIED PHYSICS LETTERS, 95(19), NOV 9 2009.
- [4] GW Sears. A GROWTH MECHANISM FOR MERCURY WHISKERS. ACTA METALLURGICA, 3(4):361–366, 1955.
- [5] R Gomer. FIELD EMISSION FROM MERCURY WHISKERS. JOURNAL OF CHEMICAL PHYSICS, 28(3):457–464, 1958.
- [6] V Ruth and JP Hirth. KINETICS OF DIFFUSION-CONTROLLED WHISKER GROWTH. JOURNAL OF CHEMICAL PHYSICS, 41(10):3139– &, 1964.

#### BIBLIOGRAPHY

- [7] JM Blakely and KA Jackson. GROWTH OF CRYSTAL WHISKERS. JOUR-NAL OF CHEMICAL PHYSICS, 37(2):428–&, 1962.
- [8] RL Parker, RL Anderson, and SC Hardy. GROWTH AND EVAPORA-TION KINETICS AND SURFACE DIFFUSION OF K AND HG CRYSTAL WHISKERS. APPLIED PHYSICS LETTERS, 3(6):93–95, 1963.
- [9] EI Givargizov. FUNDAMENTAL ASPECTS OF VLS GROWTH. JOURNAL OF CRYSTAL GROWTH, 31(DEC):20–30, 1975.
- [10] L Schubert, P Werner, ND Zakharov, G Gerth, FM Kolb, L Long, U Gosele, and TY Tan. Silicon nanowhiskers grown on ; 111 ; Si substrates by molecularbeam epitaxy. APPLIED PHYSICS LETTERS, 84(24):4968–4970, JUN 14 2004.
- [11] J Johansson, CPT Svensson, T Martensson, L Samuelson, and W Seifert. Mass transport model for semiconductor nanowire growth. JOURNAL OF PHYSI-CAL CHEMISTRY B, 109(28):13567–13571, JUL 21 2005.
- [12] VG Dubrovskii, GE Cirlin, IP Soshnikov, AA Tonkikh, NV Sibirev, YB Samsonenko, and VM Ustinov. Diffusion-induced growth of GaAs nanowhiskers during molecular beam epitaxy: Theory and experiment. *PHYSICAL REVIEW B*, 71(20), MAY 2005.
- [13] D. S. Kim, U. Goesele, and M. Zacharias. Surface-diffusion induced growth of ZnO nanowires. JOURNAL OF CRYSTAL GROWTH, 311(11):3216–3219, MAY 15 2009.

#### BIBLIOGRAPHY

- [14] Seungjun Oh, Mina Jung, Jieun Koo, Youngji Cho, Sungkuk Choi, Samnyung Yi, Gyungsuk Kil, and Jiho Chang. The mechanism of ZnO nanorod growth by vapor phase transportation. *PHYSICA E-LOW-DIMENSIONAL SYSTEMS & NANOSTRUCTURES*, 42(9):2285–2288, JUL 2010.
- [15] S. R. Hejazi and H. R. Madaah Hosseini. A diffusion-controlled kinetic model for growth of Au-catalyzed ZnO nanorods: Theory and experiment. *JOURNAL OF CRYSTAL GROWTH*, 309(1):70–75, NOV 1 2007.
- [16] Donald L. Smith. Thin-Film Deposition, Principles and Practice. McGraw-Hill, 1995.
- [17] Murray R Spiegel. Schaum's Outline of Mathematical Handbook of Formulas and Tables,. McGraw-Hill, 1998.
- [18] L. E. Froberg, W. Seifert, and J. Johansson. Diameter-dependent growth rate of InAs nanowires. *PHYSICAL REVIEW B*, 76(15), OCT 2007.

## Chapter 7

## Conclusions

This chapter summarises and discusses the work conducted in this thesis and suggests possible directions for future work in this area.

#### 7.1 Introduction and experimental work

Chapter 1 provides an introduction to the material ZnO, its potential applications and the motivation for this thesis. Chapter 2 discusses the experimental work carried out in this thesis. We prepare Si substrates for VPT growth by deposition of ZnO buffer layers to provide nucleation sites for ZnO nanowire growth. VPT growth using Zn vapour produced by the CTR of ZnO powder occurs at a growth temperature of 1200 K. VPT growth usually makes use of residual  $O_2$  in the furnace after a brief flushing period but we also describe VPT growths with the introduction of a specific amount of  $O_2$  to the gas flow. VPT growth on ZnO buffer layers results in the production of well aligned ZnO nanowires. We observe no nanowire growth on bare Si/SiO<sub>2</sub> substrates.

# 7.2 Thermodynamics of the gas atmosphere during VPT growth

The goal of Chapters 3 and 4 is to determine the possible condensing species or the pathway to the formation of solid ZnO deposits in our growth system. Solid ZnO can be formed in two ways; Zn vapour condensation followed by oxidation or ZnO molecular vapour condensation to crystalline ZnO.

In Chapter 3 we use the Gibbs free energy of reaction of the carbothermal reduction of ZnO powder to find the partial pressure and saturation of the Zn vapour produced. We find that the Zn vapour present in the furnace is always significantly undersaturated, supporting our experimental results showing that nanowire growth does not occur without suitable nucleation or accommodation sites. We also calculate the degree of saturation of Zn vapour over an already growing ZnO nanowire and find it is positive, which indicates that on an already nucleated nanowire, Zn vapour readily condenses on the nanowire and reacts with  $O_2$  to form solid ZnO. The impingement rate of Zn vapour and  $O_2$  were found to be sufficient to account for the observed nanowire growth.

Chapter 4 describes the development and application of a model to calculate the Gibbs free energy of the reaction  $\operatorname{Zn}(g) + \frac{1}{2}O_2(g) \to \operatorname{ZnO}(g)$ . Using this Gibbs free energy, we find the partial pressure of ZnO vapour present, which is relatively small, compared to the Zn vapour partial pressure discussed in Chapter 3. However, the degree of saturation of the ZnO vapour produced is large suggesting that ZnO vapour should easily condense on the growth substrates. This contradicts experimental evidence, which shows no nanowire growth without accommodation sites, suggesting an energy barrier to the nucleation of ZnO (which is examined further in Chapter

5). The impingement rate of ZnO molecules, while smaller than for atomic Zn, is still greater than that required for the growth observed at temperatures over 1000 K, indicating that both species can contribute to the growth of ZnO nanowires in VPT growth via CTR.

Based on the material in chapters 3 and 4 we suggest that the diversity of ZnO nanostructure morphologies observed experimentally in the literature may be related to the simultaneous presence of these two growth channels and their relative importance in different growth conditions. These growth channels depend on, *inter alia*, the varying temperature dependences and time-scales of surface diffusion of Zn and ZnO species and the oxidative reaction and incorporation of Zn atoms into the growing ZnO nanocrystals. This balance is likely to be a sensitive function of growth parameters, thus explaining both the diversity of nanostructure morphologies and the challenges of developing reproducible and scalable growth systems for specific applicable morphologies.

## 7.2.1 Further discussion on limitations of model used and of experimental set-up

The calculations in these two chapters make assumptions about the experimental situation that mean that the values calculated are maximum possible values, it seems probable that these far exceed the actual values in the growth system. There are various issues with the growth system that make more accurate modelling very difficult.

The actual amount of Zn vapour produced by the CTR of ZnO powder will be smaller than that predicted, due to various experimental factors. Firstly, the degree to which the carbon powder mixes with ZnO powder in the source material, and the subsequent contact between them, will impact on the efficiency of the reaction in producing Zn vapour. This is evidenced by the fact that when the samples are removed from the furnace, we observe a white crust of ZnO powder on top of the mixed powders due to re-deposition of ZnO and, this re-deposition of ZnO may block the release of further Zn vapour from the source. In combination with this reduction in Zn production, the flow of Ar through the furnace will deplet the amount of Zn vapour present, so that the assumption of a constant value of Zn vapour for the entire duration of the VPT growth is not realistic. A study of the time dependence of the partial pressure of the Zn vapour produced and the residual  $O_2$  present during the growth would greatly improve the applicability of this model to our experimental system. Similarly, an examination of the  $O_2$  concentration in the furnace during the growths where a specific amount of  $O_2$  is introduced would also be of interest. The ability to vary the amount of introduced  $O_2$  is limited by the MFC used. The value used is the smallest value possible with the equipment available. It would be beneficial to make a study on the effect of different  $O_2$  concentrations on the resulting growth and to do this a more sensitive MFC is needed.

The temperature of the furnace is assumed to reach the growth temperature and remain constant for the duration of the growth. Figure 2.7 below shows that the measured temperature of the furnace overshoots the set temperature by more than 100 K before settling to a value  $\sim 50$  K higher than the set temperature. In the initial stages this will cause a larger amount of Zn vapour to be produced. Dr. Daragh Byrne from our group in DCU has previously noted that a slow temperature ramping can avoid this overshoot [1], and further experiments examining the effect of the overshoot could give insight into the temperature dependence of Zn vapour production.

Although the work presented here is a simplified model of the growth system, it produces interesting results and provides a good first attempt at modelling the thermodynamics of the VPT growth of ZnO nanowires.

#### 7.3 Nucleation of ZnO

In chapter 5 we derive and apply a model to find the energy barrier to ZnO nucleation suggested by the results enumerated in Chapter 4. We describe the development of a model to calculate the rates of nucleation for both homogeneous and heterogeneous nucleation.

The nucleation barrier to homogeneous nucleation was found by first calculating the equilibrium size, shape and critical size of the nucleating crystal. The barrier to homogeneous nucleation is  $2.65 \text{ eV} \sim 20 \text{k}_{\text{b}}\text{T}$ . Using the derived rate of homogeneous nucleation we find the number of nucleation events in one hour, in a volume of  $1 \text{ cm} \times 1 \text{ } \mu\text{m} \times 1 \text{ } \mu\text{m}$ , which is 0.024 events.

The barrier to heterogeneous nucleation of ZnO vapour, when the lattice mismatch between the nucleating crystal and the substrate is taken into account, is found to be 8.63eV. The rate of heterogeneous nucleation events over a growth time of one hour, in an area of 1  $\mu$ m × 1  $\mu$ m, is 9.25 × 10<sup>-18</sup> events.

In these calculations, the lattice mismatch is taken to be between ZnO and Si, whereas in reality, the lattice mismatch would be larger than this value because the substrate will be silicon with a thin layer of silicon dioxide. The lattice mismatch between ZnO and SiO<sub>2</sub> is much larger and would lead to a much greater energy barrier and a lower rate of nucleation. We take the calculation for Si as a maximum possible number of nucleation events, but in an experimental situation we would expect to find a smaller number, due to the presence of the layer of  $SiO_2$ , which is always present on any sample exposed to an environment containing oxygen.

These results show that although the ZnO vapour present during the growth is supersaturated as calculated in Chapter 4, we do not expect to see ZnO nanowire growth on bare substrates. Seeds or nucleation sites where the barriers to nucleation are overcome, are required for nanowire growth for both growth pathways.

Transmission electron microscope (TEM) images of ZnO nanowires grown in our group reported by Dr. Daragh Byrne *et al.* (as shown in Figure 7.1) show small ZnO particulates embedded in the base of nanowires [1]. The size of these particulates are larger than the critical size of homogeneous nuclei predicted by our model. Future research might explore the growth rate of homogeneously formed nuclei in the space between the source powder material and sample and find the average size of such nuclei by the time they reach the substrate surface and compare this size with the size of the observed particulates.



Figure 7.1: TEM images (acquired by Rabie Fath Allah, Teresa Ben and David Gonzalez Robledo, UCA Cadiz) of ZnO nanowires grown by Dr. Daragh Byrne [1]

## 7.4 Growth rate of ZnO nanowires

Chapter 6 examines the growth rate and radius-dependence of the length of ZnO nanowires grown by VPT. A model developed by Johansson [2] is slightly altered to to take account of the different morphology observed in our grown nanowires, with flat top surfaces, compared to those with the rounded top surfaces considered

by the original model. The model includes contributions of molecules from direct impingement onto the top of the nanowire and molecules diffusing from the sidewalls and from the substrate. This model predicts that the nanowire length increases with decreasing nanowire radius.

The results of this model are compared to our experimentally measured dimensions of ZnO nanowires and overall good agreement is obtained. These results show an inverse relationship between the length of the nanowire and the radius supporting the inclusion of molecules diffusing from the sidewalls in the model.

There are also issues to be addressed in the application of this model to our growth system. In the derivation of the model, it is assumed that the interwire spacing of the nanowires is large, which allows us to claim that the impingement of atoms/molecules onto the top of the wire is equal to the impingement of atoms/molecules on the sidewalls. As can be seen in the SEM images of the samples used, the nanowire density on most samples is large, indicating that the impingement rate of molecules on the sidewalls is less than the impingement rate of molecules onto the top of the ordered arrays of nanowires grown in our group by Seamus Garry [3]. These array templates are produced by nanosphere lithography and make hexagonally patterned SiO<sub>2</sub> array templates for VPT growth to produce arrays of ZnO vertical nanowires, with larger interwire spacings of 500 nm, 1  $\mu$ m, 1.5  $\mu$ m. Figure 7.2 shows nanowires grown on nanowire arrays with a spacing of 1.5  $\mu$ m. These larger interwire spacings would reduce the effects of shadowing and allow a better direct comparison of experimental results with the theoretical model.



Figure 7.2: ZnO nanowires grown via VPT on spaced nanowire arrays with 1.5  $\mu m$  spacing, provided by Seamus Garry

Furthermore, the nanowires grown on these arrays tend to have almost identical radii determined by the available contact points to the underlying buffer layer. Measurements of nanowires grown on these arrays would provide interesting results, as one would expect to find more uniform lengths throughout; using arrays of different spacing could provide more points to work out fitting parameters like the molecular diffusion length. Figure 7.3 shows preliminary measurements of ZnO nanowires grown via VPT on spaced nanowire arrays with 1.5  $\mu$ m spacing, provided by Seamus Garry shown above in Figure 7.2. This plot shows a much smaller range of nanowire lengths and radii than observed on ZnO buffer layers.



Figure 7.3: Preliminary measurements of nanowire length as a function of radius for ZnO nanowires grown via VPT on spaced nanowire arrays with 1.5  $\mu$ m spacing, provided by Seamus Garry

We also assume in the model that the radius of the nanowire is constant throughout the growth, but this is not always the case. We observe tapered nanowires (as shown in Figure 7.1) and have even observed nanowires with two distinct radii (Figure 7.4). It would be very interesting to further study the issue of radial growth in the model and introduce a non constant radius into the model.



Figure 7.4: ZnO nanowires grown via VPT showing two different radii, provided by Dr. Daragh Byrne [4]

## 7.5 Conclusion

This thesis discusses the growth atmosphere, condensing species and nucleation conditions relevant to vapour phase transport growth of ZnO nanowires. The partial pressure of molecular ZnO in a  $Zn/O_2$  mix at normal ZnO growth temperatures is much lower than that of the Zn partial pressures. In typical vapour phase transport growth conditions, using carbothermal reduction, the Zn vapour is always undersaturated while the ZnO vapour is always supersaturated. In the case of the ZnO vapour, our analysis suggests that the barrier to nucleation is too large for nucleation of ZnO to take place, which is consistent with experimental evidence that ZnO nanowires will not grow on bare Si/SiO<sub>2</sub> substrates. In the presence of suitable accommodation sites, growth can occur via Zn vapour condensation (followed by oxidation) and via direct condensation of molecular ZnO. The balance between these two condensing species is likely to be a sensitive function of growth parameters.

This thesis also examines the relationship between the length and radius of ZnO

nanowires grown via VPT and finds that the lengths of the nanowires increase with decreasing radius, supporting the inclusion of a diffusion term in a model for the incorporation of molecules into a growing nanowire.

We believe the work done in this thesis could be fruitfully expanded in two ways; the first, relating to the theoretical models of ZnO growth and the second, experimental in nature. The models could be improved by introducing a time dependence of the Zn and  $O_2$  vapour present in the furnace, dealing with the variation in growth temperature during the growth and addressing the issue of radial growth. Current experiments in ZnO nanowire growth could be furthered by using a slower temperature ramp pattern, finer control of the amount of introduced  $O_2$  and making use of spaced nanowire arrays. By refining our models of ZnO nanowire growth we would more accurately reflect the experimental situation and see more accurate predictions of ZnO morphology. The experiments, in tandem with this, would give us yet more information upon which to further improve our models.

## Bibliography

- [1] Daragh Byrne, Rabie Fath Allah, Teresa Ben, David Gonzalez Robledo, Brendan Twamley, Martin O. Henry, and Enda McGlynn. Study of Morphological and Related Properties of Aligned Zinc Oxide Nanorods Grown by Vapor Phase Transport on Chemical Bath Deposited Buffer Layers. CRYSTAL GROWTH & DESIGN, 11(12):5378–5386, DEC 2011.
- [2] J Johansson, CPT Svensson, T Martensson, L Samuelson, and W Seifert. Mass transport model for semiconductor nanowire growth. JOURNAL OF PHYSI-CAL CHEMISTRY B, 109(28):13567–13571, JUL 21 2005.
- [3] E. McCarthy, S. Garry, D. Byrne, E. McGlynn, and J. P. Mosnier. Field emission in ordered arrays of ZnO nanowires prepared by nanosphere lithography and extended Fowler-Nordheim analyses. *JOURNAL OF APPLIED PHYSICS*, 110(12), DEC 15 2011.
- [4] D. Byrne, E. McGlynn, M. O. Henry, K. Kumar, and G. Hughes. A novel, substrate independent three-step process for the growth of uniform ZnO nanorod arrays. *THIN SOLID FILMS*, 518(16, Sp. Iss. SI):4489–4492, JUN 1 2010.

# Appendix A

# Appendix: MATLAB programs

## A.1 MATLAB program to calculate Gibbs free energy of ZnO

format short e

% Temperatures range

t=(100:100:6000)';

% room temp

rt=298.15;

% constants

h=6.62606896e-34;

hb=1.054571628e-34;

kb=1.3806504e-23;

kbt=kb\*t;

r = 8.314472;

h=6.62606896e-34;

u=1.660538782e-27;

c=299792458; cdk=c/kb p=1.01325e5; pdkbt=p./kbt; cmm1=1.9865e-23;

% variables for molecule

m1=15.99\*u; m2=65.37\*u; m=m1+m2; rad=1.719e-10;v0=7.27e4;

sig=1

% electronic energy levels

$$g0=1;$$
  
 $g1=6;$ 

% converting energy level from cm-1 to J

```
delecm=2097.0407;
dele=delecm.*cmm1./kb
```

delecm 2=5060;

d0 = 157e3;

 $rs=rad.\hat{2};$ 

% lt is thermal wavelength

 $ltsb{=}kb^{*}m^{*}t;$
lts=ltsa./ltsb; lt=lts.0.5; ltc=lt.3;

% mu is reduced mass.

mu=m1\*m2./m;

% I is the moment of inertia.

I=mu\*rs;

% tr is rotation temp-theta rot.

```
den=4*pi*c*I;
```

b=hb./den

tr=cdk\*h\*b;

rott=tr./t;

% tv is vibration temp- theta v

```
freq=v0;
```

tv=cdk\*h\*freq;

vibt=tv./t;

% electric contribution

elect=dele./t;

g1e=g1.\*exp(-elect);

elec=g0+g1e

elech=dele.\*g1e

elecwh=elech./elec;

elecs=elect.\*g1e

varelec=elecs./elec;

% putting it all together

```
var1=pdkbt.*ltc.*rott.*sig;
var2=1-exp(-vibt);
var3=exp(vibt)-1;
var4=(var3).^1;
var4sq=var4.*var4;
var5=exp(-vibt)./var2;
```

% entropy

stZnO=3.5\*r-r\*log(var1)-r\*log(var2)+r.\*vibt.\*var4+r.\*log(elec)+r.\*varelec;

% gibbs free energy

```
gtZnO1=r.*t.*log(var1)+r.*t.*log(var2)-r.*t.*log(elec)-d0;
```

% enthalpy

htZnO1=3.5.\*r.\*t+r.\*tv.\*var5+r.\*elecwh-d0;

entropy1=[t stZnO];

gibbZnO1 = [t gtZnO1];

enthalpyZnO1 = [t htZnO1];

xlswrite('ZnO.xls', entropy1, 'entropy', 'A1')

xlswrite('ZnO.xls', gibbZnO1, 'gibbZnO','A1')

xlswrite('ZnO.xls', enthalpyZnO1, 'enthalpy','A1')

## A.2 MATLAB program to calculate equillibrium constant for ZnO reaction

% read in values for ZnO

nadataZnO = xlsread('ZnO.xls', 'gibbZnO'); gibbZnO=[t gtZnO];

% read in values for O2

nadataZnO = xlsread('o2.xls', 'gibbO2');

gibbO2 = [t gtO2];

% read in values for Zn

nadataZnO = xlsread('Zn.xls', 'gibbZn');

gibbZn=[t gtZn];

% calculate the gibbs free energy of reaction

```
gr=gtZnO-0.5*gtO2-gtZn;
grdiff=[t gr1]
```

xlswrite('reaction1.xls', grdiff, 'grdiff', 'A1')

% calculate the equillibrium constant

r=8.314472; rtemp=r\*t; gdrt=gr./rtemp; kcn=exp(-gdrt); kp=[t kc1] xlswrite('reaction1.xls', kp,'kp','A1')

## A.3 MATALB program to calculate the partial pressure of Zn produced by CTR

format short e % read in Gibbs free erngy of reaction for CTR

grth= xlsread('gibbreac.xls', 'gibb')

```
t = xlsread('gibbreac.xls', 'temp')
```

d=grth./t

% input calculated partial pressures of oxygen and argon from MFC

po2=3.268387e3;

par=9.8052e4;

% constants

hb=1.054571628e-34;

kb=1.3806504e-23;

r = 8.314472;

h=6.62606896e-34;

```
u=1.660538782e-27;
```

```
c = 299792458;
```

m = 65.37;

% for temperatures below 1000 K

for i = (1:7);

% calculate the equilibrium constant

rtemp(i)=r.\*t(i); grta(i)=1.\*grth(i); gdrt(i)=grta(i)./rtemp(i);

kczn(i) = exp(-gdrt(i));

```
kctt(i)=kczn(i).\hat{0}.66666666;

p(i)=1.2599.*kctt(i);

pun(i)=p(i).*1e5;

% normalize to keep total gas at 1 atm.

den(i)=po2+par+1.5.*pun(i);

pzn(i)=pun(i)*1.0132e5/den(i);

pO2(i)=po2.*1.0132e5/den(i);
```

end

% for temperatures above 1000 K

for j = (8:18);

```
rtemp(j)=r.*t(j);

grtb(j)=1.*grth(j);

gdrt(j)=grtb(j)./rtemp(j);

kczn(j)=exp(-gdrt(j));

p(j)=(kczn(j)).\hat{0}.5;

pun(j)=p(j).*1e5;

tem=t(j);

% normalize to keep total gas at 1 atm.

den(j)=po2+par+2.0.*pun(j);

pzn(j)=pun(j)*1.0132e5/den(j);

pO2(j)=po2.*1.0132e5/den(j);
```

end

 $\operatorname{temp}=t$ 

 $\rm kcznn=kczn$ 

kpzn=[temp kcznn'] xlswrite('carbo', kpzn,'kpzn','A1') pznn=pzn; pznt=[t pznn']; pO2t=[t pO2'];punzn=[t pun']; xlswrite('carbo', pznt,'pznt','A1') xlswrite('carbo', pO2t,'pO2t','A1') xlswrite('carbo', punzn,'punzn','A1') % to find impingement flux for zn mmt=m\*t  $d=mmt.\hat{0}.5$ pz=pznn.\*2.63e20 jp=pz'./d % this gives j in mc/m2s j=jp\*1e+4;

#### A.4 MATLAB program to calculate partial pressure of ZnO

format short e

% read in equilibrium constant

ndata= xlsread('reaction1.xls', 'kp')
t = ndata(:,1);
kc=ndata(:,2);

% read in partial pressure of Zn vapour and O2 vapour

```
ndatazn=xlsread('carbo.xls','pznt')
ndatao2=xlsread('carbo.xls','pO2t')
pzn=ndatazn(:,2)
po2=ndatao2(:,2)
t=ndatazno(:,1)
ps=(po2./1e5).0.5
pznp=pzn./1e5
pp=ps.*pznp;
```

% calculate ZnO partial pressure

```
pzno=kc.*pp.*1e5;
pzno=[t pzno]
xlswrite('pressure.xls', pzno, 'pzno','A1')
```

% calculate impingement flux for zno

```
mm=81.36;
mmt=mm*t
d=mmt.0.5
pznot=pzno.*2.63e20;
```

jp=pzno./d jp4=pzno4t./d % this gives j in mc/m2s j=jp\*1e+4; jzno=[t j3] xlswrite('pressure',jzno,'jzno','A1')

#### A.5 MATLAB programs to calculate vapour pressure of ZnO

## A.5.1 To find the vapour pressure of Zn vapour over solid ZnO

format short e

% read in values from database of gibbs free energy of reaction for production of Zn vapour from

grth= xlsread('gibbelling.xls', 'grt');

t = xlsread('gibbelling.xls', 'temp');

% calculate the equillibrium constant

```
r=8.314472 ;

rtemp=r*t;

gdrt=grth./rtemp;

kc1=exp(-gdrt);

kp1=[t kc1];

xlswrite('solidZnO', kp1,'kp1','A1')

% calculate the vapour pressure of Zn
```

 $twopthird = 2\hat{0}.3333;$ 

# A.5.2 Using the vapour pressure of Zn vapour, to find the vapour pressure of ZnO

format short e

% read in vapour pressure of Zn over Solid ZnO

ndata=xlsread('solidZnO','pressureznpa')

pressurez = [t pznpa];

#### % read in equilibrium constant for reaction to produce ZnO vapour

```
ndatak= xlsread('reaction1.xls','kp')
kcn=ndatak(:,2);
pzn=pznpa./1e5
po2=0.5.*pznpa./1e5;
ps=(po2).0.5;
pp=ps.*pzn;
vpznon=kcn.*pp.*1e+5;
vpzno=[t vpznon]
xlswrite('solidZnO', vpzno,'pressureznog','A1')
```

## A.6 MATLAB program to calculate the degree of saturation of ZnO vapour

format short

% read in partial pressure of ZnO

nadata=xlsread('pressure.xls','pzno');

t=nadata(:,1);

pznon=nadata(:,2);

% read in vapour pressure of ZnO

ndata=xlsread('solidZnO','pressureznog');

t = ndata(:,1);

vpznon=ndata(:,2);

% calculate degree of saturation

```
simm=pznon-vpznon;
sim=simm./vpznon;
deg=[t sim]
xlswrite('degreezno.xls',deg, 'degree','A1')
```

## A.7 MATLAB program to calculate rate of homogeneous nucleation

% calculate energy barrier to homogeneous nucleation. format short e

% constants

hb=1.054571628e-34;

kb=1.3806504e-23;

r = 8.314472;

h=6.62606896e-34;

u=1.660538782e-27;

c=299792458;

cdk=c/kb;

% values for ZnO

mass=81.37; m=mass\*u; rho=5.606e3; sur=3.2; vol=14.52e-6; rhop=1.15; rhob=2.0; rhobsqrt=rhob $\hat{0}.5$ ;

% read in partial pressure and vapour pressure of ZnO

nadata=xlsread('pressure.xls','pzno');

t=nadata(:,1);

pzno=nadata(:,5)

```
ndata=xlsread('solidZnO','pressureznog');
t=ndata(:,1);
vpznon=ndata(:,5);
kbt=kb.*t;
x=pzno./vpznon
lx=log(x);
rtlx=r.*t.*lx;
rtlx2=rtlx.*rtlx;
volsq=vol.2;
surc=rhob*rhop*rhop;
sq3=3.0.5
delgmax=(16.*sq3.*surc.*volsq)./(rtlx2);
maxgibb=[t delgmax];
xlswrite('nucleation3.xls', maxgibb, 'maxgibb','A1')
```

% calculate the rate of nucleation

$$a=pzno./(kb.*t);$$
  

$$asq=a.\hat{2};$$
  

$$b=2.*m./(pi*pi*sq3);$$
  

$$bsqrt=b.\hat{0}.5$$
  

$$au=[t asq]$$
  

$$e=asq.*bsqrt./rho;$$
  

$$f=2*rhob/rhop;$$
  

$$o=1+f;$$
  

$$w=rhop/rhobsqrt;$$

ru=o\*w
gdkbt=delgmax./kbt;
nucl=e.\*w.\*o.\*exp(-gdkbt);
nuc=[t nucl]
xlswrite('nucleation3.xls', nuc, 'nuc','A1')

#### A.8 MATLAB program to calculate the rate of heterogeneous nucleation

% calculate the barrier to heterogeneous nucleation.

format short e

% constant

hb=1.054571628e-34; kb=1.3806504e-23; r = 8.314472; h=6.62606896e-34; u=1.660538782e-27; c=299792458; cdk=c/kb;NA = 6e23;ld=1e-6;ahop=0.3e-9;No=1e19;% values for ZnO mass = 81.37; $m = mass^*u;$ rho=5.606e3; vol=14.52e-6;rhop=1.15; rhob=2.0;rhobsqrt=rhob0.5;

```
Y = 100e9;
        ep=0.4;
\% read in partial pressure and vapour pressure of ZnO
        nadata=xlsread('pressure.xls','pzno');
        t = nadata(:,1);
        pzno=nadata(:,5)
        ndata=xlsread('solidZnO','pressureznog');
        t = ndata(:,1);
        vpznon=ndata(:,5);
        kbt=kb.*t;
        x=pzno./vpznon
       lx = log(x);
        rtlx=r.*t.*lx;
        rtlx2=rtlx.*rtlx;
        volsq=vol.\hat{2};
        surc=rhob*rhop*rhop;
        sq3=3.0.5
                     parta = (8.*sq3.*surc);
        denb=2.*rtlx-vol.*Y.*ep.*ep;
        partb = (2.*vol)./denb;
        partb2=partb.*partb;
        partb2i=1./partb2;
        delgmax=parta.*(partb2);
        maxgibb=[t delgmax];
        xlswrite('nucleation3het.xls', maxgibb, 'maxgibb','A1')
```

% to find the rate of nucleation

po=3\*pi\*kb.\*t
posq=(po).0.5;
Z=0.5.\*(1./(sq3\*8)0.5)\*vol\*(1./NA)\*(1./rhop)\*(1/(rhob)0.5).\*(partb2i./(posq));
denj=2.\*pi.\*m.\*kb.\*t;
denjsq=(denj).0.5
terj=pzno./denjsq;
omega=8.\*sq3.\*terj.\*4.\*ld.\*ld\*(1/ahop)\*rhop.\*partb;
Kh=omega.\*Z.\*No
gdkbt=delgmax./kbt;
nucl=Kh.\*exp(-gdkbt);
nuc=[t nucl]
xlswrite('nucleation3het.xls', nuc, 'nuc','A1')

A.9 MATLAB program to calculate growth rate and nanowire length as a function of radius

#### A.9 MATLAB program to calculate growth rate and nanowire

#### length as a function of radius

format short e

% diffusion lengths, molecular volume

lamda=100e-9;

lamdas=100e-9

molvol=2.541065e-29;

% input impingment rate: T=1200K

j=0.85e19;

% for different radii

for n = (1:1:20)

```
rw=20e-9+n*10e-9
lamr=lamda/rw;
lamrs=rw/lamdas;
%to calculate jsw
K0 = besselk(0,lamrs);
K0rq = besselk(0,lamrs);
K1= besselk(1,lamrs);
ratio=K1./K0;
jsw=-j.*lamdas.*ratio;
%for time
time=0;
L=0;
```

A.9 MATLAB program to calculate growth rate and nanowire length as a function of radius

```
\operatorname{count}=1;
for k=0:1:180
             step=10;
             time=10^{*}k;
             l=L./lamda;
             ta = tanh(l);
             co = cosh(l);
             a=2*molvol.*j.*lamr.*ta;
             b1=2*molvol*jsw;
             b2 = rw^*co;
             b=b1/b2;
             c=molvol*j;
             tempLdot=a+c-b;
             L=tempLdot*step*(count-1);
             o(count, 1) = time;
             o(count,2)=L;
             Ldot(count)=tempLdot;
             count=count+1;
end
term1(n,1) = rw*1e9;
term1(n,2) = c*1e9;
term2(n,1) = rw*1e9;
```

term2(n,2) = a\*1e9;

## A.9 MATLAB program to calculate growth rate and nanowire length as a function of radius

```
term3(n,1)=rw*1e9;
term3(n,2)=b*1e9;
xlswrite('Lengthrad2', o,'lengthsub','A1')
xlswrite('Lengthrad2', term1,'term1','A1')
xlswrite('Lengthrad2', term2,'term2','A1')
xlswrite('Lengthrad2', term3,'term3','A1')
e(n,1)=rw;
e(n,2)=L;
g(n,1)=rw;
g(n,2)=tempLdot;
```

 $\operatorname{end}$ 

xlswrite('Lengthrad2', e,'length','A1')

xlswrite('Lengthrad2', u,'lengthnm','A1')