

Transparent conducting aluminium doped zinc oxide for silicon quantum dot solar cell devices in third generation photovoltaics

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# Transparent Conducting Aluminium Doped Zinc Oxide for Silicon Quantum Dot Solar Cell Devices in Third Generation Photovoltaics

Author: Terry Chien-Jen Yang Joint-supervisors: Gavin Conibeer Ivan Perez-Wurfl

> Co-supervisor: Martin Green

A THESIS SUBMITTED TO THE GRADUATE RESEARCH SCHOOL IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY



Australian Centre for Advanced Photovoltaics School of Photovoltaic and Renewable Energy Engineering Faculty of Engineering University of New South Wales

> SYDNEY, AUSTRALIA AUGUST, 2015

ii

### **Thesis/Dissertation Sheet**

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Thesis/I	Dissertation Sheet	
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Abstract 350 words	s maximum: (PLEASE TYPE)	
Silicon quantum dots (QDs), a subset of Si nanocrystals (NCs), in o third generation photovoltaics, which aim to cost effectively exceed to were fabricated by magnetron sputtered thin film superlattice bilayer 1100 °C. The annealing causes solid-state nucleation and subseque type of Si NC material is its poor carrier transport and material qualit high series resistance despite their reasonable open-circuit voltages	dielectric matrices with bandgap tunability the Shockley-Queisser limit of efficiency. s of silicon rich oxide (SRO) and silicon di ient formation of Si NCs in the SRO laye ty. Solar cell devices in the past have exp up to 492 mV.	y are promising thin film materials for The Si QDs investigated in this thesis ioxide (SiO <sub>2</sub> ) followed by annealing at rs. However, the main issue with this verienced heavy current crowding and
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#### Abstract

Silicon quantum dots (QDs), a subset of Si nanocrystals (NCs), in dielectric matrices with bandgap tunability are promising thin film materials for third generation photovoltaics, which aim to cost effectively exceed the Shockley-Queisser limit of efficiency. The Si QDs investigated in this thesis were fabricated by magnetron sputtered thin film superlattice bilayers of silicon rich oxide (SRO) and silicon dioxide (SiO<sub>2</sub>) followed by annealing at 1100 °C. The annealing causes solid-state nucleation and subsequent formation of Si NCs in the SRO layers. However, the main issue with this type of Si NC material is its poor carrier transport and material quality. Solar cell devices in the past have experienced heavy current crowding and high series resistance despite their reasonable open-circuit voltages up to 492 mV.

Aluminium doped zinc oxide (AZO) is a promising transparent conducting oxide (TCO) which is often used in thin-film solar cells as transparent contacts. From the literature surveyed, AZO has never been used to make Si NC solar cell devices before. The key advantage of AZO is its high melting point of 1975 °C, which is much higher than other common TCOs. This allows AZO to be annealed at 1100 °C together with the SRO/SiO<sub>2</sub> bilayers, although the structural, electrical and optical properties of the AZO thin films change after annealing. The main issue is the heavy decrease in conductivity and cross-diffusion of elements.

For the first time, nucleation of Si NCs in SRO/SiO<sub>2</sub> bilayers was observed in real-time via an aberration-corrected high resolution transmission electron microscope with *in situ* heating up to 600 °C. This particular experiment showed that nucleation of Si NCs begins at an unexpectedly low temperature (450 °C) which suggests that *ex situ* annealing at 1100 °C may not be necessary. However, through external furnace annealing temperature dependence experiments later it was shown that the higher the annealing temperature, the better the extent of crystallisation of the Si NCs. The advantages of high Si content SRO/SiO<sub>2</sub> bilayer superlattices with boron and phosphorus doping were also investigated. It was also shown that AZO forms a good ohmic contact to both the high Si content B and P doped SRO/SiO<sub>2</sub> bilayer superlattices. Finally, together with utilising AZO as a transparent contact, a prototype superstrate configured Si NC solar cell device is demonstrated.

### Acknowledgements

I have always likened completing a PhD to running a marathon. Instead of running 42 km it has taken me a little over 4 years. All the research and thesis writing has certainly been quite the challenge, especially in these last few months. Just like running a marathon, the last few kilometres are the hardest as you test yourself to the limits as you edge closer towards the finish line. I would like to express my gratitude to those that have helped me along the way.

First of all I would like to thank my supervisors, Prof. Gavin Conibeer and Dr. Ivan Perez-Wurfl for their academic guidance, fruitful discussions and mentoring. During the course of my PhD study through my supervisors I have learnt how to conduct scientific research, write scholarly articles and contribute to the wider academic community. Most of all I respect their patient, considerate and understanding nature which has helped me through these 4 years. To my co-supervisor Scientia Prof. Martin Green, you have been such an inspiration to me as a researcher in the field of photovoltaics and I hope the world will continue to embrace solar energy in the future.

I would also like to express my gratitude to my colleagues in the third generation all-Si QD tandem solar cells group: Dr. Binesh Puthen-Veettil, Dr. Dawei Di, Lingfeng Wu, Ziyun Lin, Tian Zhang, Xuguang Jia and Keita Nomoto. I will always remember the countless hours spent in the laboratories at Bay Street, the Electrical Engineering and Tyree Energy Technologies Buildings. The most memorable moments being with the AJA sputtering system. It has been such a great honour to work alongside a group of such unselfish, dedicated and amazing people.

As an aside, I also spent a four month student research exchange at the Technion – Israel Institute of Technology, partially funded by the Australian Israel Scientific Exchange Foundation (AISEF), which has resulted in my first published journal article. Therefore I wish to thank my supervisor at the time, Prof. Avner Rothschild dearly for his benevolence and generosity. I would also like to thank Dr. Yaron Kauffmann for the research work we conducted with the FEI Titan 800-300 keV FEG S/TEM system. Furthermore, I would like to acknowledge the colleagues and friends from my wonderful research exchange: Irina Dumchin, Michael Kalina, Oshri Blank, Moran Koren, Tzipi Cohen-Hyams, Joel Czarny, Gadi Saper, Roy Pinhassi, Hen Dotan and many others.

Returning to the University of New South Wales, I would also like to give special thanks to the lecturers, A/Prof. Alistair Sproul and Dr. Santosh Shrestha whom I have tutored courses for. Thank you very much for giving me the opportunity to teach, as I believe teaching is an essential and important part of being a PhD student. You learn the way to speak confidently in front of a class of students, mark assignments and exam papers as well as learn how to explain the course content effectively to pass on knowledge.

To all the technicians, I would like to thank: Alan Yee for such great management of the characterisation laboratories and running many training sessions on the characterisation equipment for SPREE; Dr. Patrick Campbell, Dr. Tom Puzzer and Mark Griffin for managing and maintaining the AJA sputtering tool and other equipment (special thanks goes to Tom for switching on the forming gas for me on numerous occasions); Dr. Craig Johnson for maintaining the INTERCOVAMEX H2 thermal evaporator; Dun Li for photolithography; from the Solid State & Elemental Analysis Unit: Dr. Yu Wang for his expertise on the XRD system and Dr. Bill Gong for his XPS and ToF-SIMS measurements.

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Prem Mahinder, Byron Brown, Ravi Koghar, Mehbub Kahir, Denise Goldmann, Jimmy Niddrie, Jim Moustakis, Blayne Whiteman, Tony Tse and many others. I would also like to thank all the new friends that I made at Colombo House over the final 18 months (there are too many of you to name); you have all made the living at college era of my life more colourful and diverse. Special thanks to Colombo Dean Michael Patoka for being so understanding and accommodating during my final semester. Finally a special acknowledgement goes to Dr. Tom Jones for such progressive and expert counselling over the last 5 years. I can honestly say I would not have completed this PhD if it were not for your help. My sincere apologies if I have left anyone out of this acknowledgement.

Lastly I would like to thank my parents, sister and extended family for such understanding, patience and unconditional love through such a challenging period in my life. I hope your support will not go unrewarded and I shall always be there for all of you in the future.

Dedication

To my dearest family and friends

### Preface

This thesis is written for the fulfilment of the requirements for the degree of doctor of philosophy in photovoltaic and renewable energy engineering at the University of New South Wales Australia. The author's candidature dates from 18<sup>th</sup> July 2011 to 31<sup>st</sup> August 2015 with a period totalling to approximately 4 years. The research work was mostly conducted at the School of Photovoltaic and Renewable Energy Engineering which is the head node of the Australian Centre for Advanced Photovoltaics. Some research work was also conducted at MIKA, the Electron Microscopy Centre of the Materials Science and Engineering Faculty at the Technion – Israel Institute of Technology in Israel during the author's 4 month research exchange from November 2012 to March 2013.

This preface was written in hopes of improving the readability of the thesis.

It is assumed that readers should have a reasonable knowledge of photovoltaics and solar cells as well as a background in fundamental physics. The overall technical content and main findings have already been outlined in the abstract. Furthermore, as this thesis is based on third generation all-Si quantum dot material, a large proportion of the research leans heavily towards materials characterisation. So ideally the reader should also have some background in common materials characterisation techniques. In summary, this thesis combines two major topics: silicon quantum dots for third generation photovoltaics and transparent conducting aluminium doped zinc oxide (AZO). Some research work undertaken during the author's 4 year candidature have been omitted from this thesis to maintain consistency and length. These topics were namely optical emission spectroscopy for monitoring the magnetron sputtering set-up and sol-gel spin coated AZO thin films as an alternative to magnetron sputtered AZO thin films. Also critical equipment was unavailable for extended time due to the transition between the old Electrical Engineering building to the new Tyree Energy Technologies Building (TETB) between late-2013 to 2014. The AJA sputtering system was unavailable for more than 11 months during its transfer from the Bay Street facility to the TETB.

This thesis consists of 9 chapters with the individual chapter outline presented at the end of Chapter 1. Some chapters are based on work that has already been published by the author and colleagues either in referred journal publications or as conference proceedings. The citations are based on the generic IEEE numbering style. All acronyms in the thesis are introduced when used for the first time in each new chapter. There is a list of Figures and Tables, a list of Symbols, Abbreviations and Nomenclature and a Full Reference List at the end of this thesis for your reference. The author hopes that the reader will have a clear, enjoyable and fruitful experience when reading this thesis. A list of Unique Contributions from the work in this thesis is presented on the next page.

### **Unique Contributions**

- Observed for the first time, the solid-state nucleation of silicon nanocrystals (Si NCs) in SRO/SiO2 bilayers in real time via an aberration corrected high resolution transmission electron microscope (HRTEM) with *in situ* heating up to 600 °C.
- 2) Investigated the dependence of annealing temperature up to 1100 °C on Si NC formation in SRO/SiO<sub>2</sub> bilayer superlattice thin films (although, similar experiments have been done for Si NCs from plasma enhanced chemical vapour deposition (PECVD) and for Si nitrides and carbides). It was shown that the higher the annealing temperature, the better the extent of crystallisation of the Si NCs.
- 3) Investigated the use and advantages of high Si content SRO in SRO/SiO<sub>2</sub> bilayer superlattice thin films used in the fabrication of Si NCs. High Si content SRO tends to produce thin films with lower resistivity and higher absorption cross-sections which are better properties for fabricating Si QD solar cell devices. The effects of boron and phosphorus doping on the properties of high Si content SRO/SiO<sub>2</sub> bilayers were also studied.
- 4) Investigated the structural, electrical and optical properties of transparent conducting aluminium doped zinc oxide (AZO) thin films annealed at temperatures up to 1100 °C. A special method was developed so that the thin film AZO samples could retain their conductive nature to within approximately 2 to 3 orders of magnitude after annealing in the absence of oxygen. This result may also have various applications outside of photovoltaics.
- 5) Demonstrated that AZO forms a good ohmic contact to both the high Si content B and P doped SRO/SiO<sub>2</sub> bilayer superlattices.
- 6) Conceptualised the first Si QD/NC *n-i-p* superstrate configured solar cell using AZO as a transparent conducting layer. AZO is often used as a transparent conducting layer for thin-film amorphous Si and CIGS solar cells although AZO has never been investigated in the device structure of Si NC solar cells due to the high temperature annealing step for Si NCs that is required.

## **Table of Contents**

Thesis/Dissertation Sheet	. iii
Originality Statement	.iv
Copyright Statement	. v
Abstract	.vi
Acknowledgements	vii
Dedication	. x
Preface	.xi
Unique Contributions	xiii
Table of Contents	xiv
Epigraph	xix
CHAPTER ONE: INTRODUCTION, MOTIVATION, AIMS AND OBJECTIVES	. 1
1.1 Third Generation Photovoltaics	. 1
1.2 All-Si Tandem Solar Cells	. 4
1.3 Thesis Objectives	. 6
1.4 Thesis Chapter Outline	. 6
CHAPTER TWO: BASIC THEORY OF SILICON QUANTUM DOTS AND WORK TO	
DATE	. 9
2.1 Introduction	. 9
2.2 Quantum Confinement in Si QD Nanostructures	. 9
2.3 Carrier Tunnelling Transport in Si QD Superlattices	12
2.4 Fabrication of Si QD Nanostructures and the SRO/SiO <sub>2</sub> Superlattice Structure	14
2.5 Effect of Silicon Rich Oxide Stoichiometry on the Properties of Si QD	
Superlattice Structures and the Size and Density Control of Si QDs	18
2.6 Doping of Si QD Nanostructures	21
2.7 Doping Characteristics of Silicon QD Superlattice Structures	26
2.8 Summary	29
CHAPTER THREE: PROPERTIES OF TRANSPARENT CONDUCTING ALUMINIUM	
DOPED ZINC OXIDE	31
3.1 General Overview of Transparent Conducting Oxides	31
3.2 Introduction to Zinc Oxide	33
3.2.1 A Brief History and Applications of ZnO	33

3.2.2 Basic Structural, Physical and Optical Properties of ZnO	33
3.2.3 Electrical Properties of ZnO	35
3.2.4 Extrinsic Doping of ZnO	41
3.2.5 Carrier Transport Properties in Polycrystalline ZnO Thin films	43
3.2.6 Types of Deposition Methods	44
3.3 Summary	45
CHAPTER FOUR: FABRICATION AND CHARACTERISATION TECHNIQUES	46
4.1 Introduction	46
4.2 Fabrication Techniques	46
4.2.1 RF Magnetron Sputtering	46
4.2.2 Furnace Annealing	48
4.2.3 Metallisation	48
4.3 Materials Characterisation Tools	49
4.3.1 Transmission Electron Microscopy	49
4.3.2 Scanning Electron Microscopy	51
4.3.3 Atom Force Microscopy	51
4.3.4 X-ray Diffraction	52
4.3.5 X-ray Photoelectron Spectroscopy	53
4.3.6 Time-of-Flight Secondary Ion Mass Spectrometry	54
4.3.7 Raman Spectroscopy	55
4.3.8 Spectrophotometry (Reflection, Transmission and Absorption)	56
4.3.9 Spectroscopic Ellipsometry	57
4.3.10 Photoluminescence	58
4.3.11 Four-Point Probe and Hall Measurements	59
4.4 Photovoltaic Device Characterisation Tools	61
4.4.1 Suns-V <sub>oc</sub> (Quasi-steady-state Open-circuit Method)	61
4.4.2 DarkStar I-VTester	62
CHAPTER FIVE: IN SITU HIGH RESOLUTION TRANSMISSION ELECTRON	
MICROSCOPY OF SILICON NANOCRYSTAL NUCLEATION IN A SIO $_2$	
BILAYERED MATRIX	64
5.1 Introduction	64
5.2 Experimental Details	65

5.4 Conclusion	74
CHAPTER SIX <sup>1</sup> STUDY OF HIGH SILICON CONTENT SRO/SIO <sub>2</sub> BILAYER	
SUPERI ATTICE THIN FILMS WITH BORON AND PHOSPHORUS DOPING	75
6.1 Introduction	75
6.2 Experimental Details	76
6.3 Results and Discussion	77
6.3.1 Grazing Incidence X-Ray Diffraction	77
6.3.2 High Resolution and Energy Filtered Transmission Electron Microscopy	81
6.3.3 Raman Spectroscopy	85
6.3.4 Photoluminescence	88
6.3.5 Electrical Measurements	90
6.4 Conclusion	91
CHAPTER SEVEN: ANNEALING TEMPERATURE AND TREATMENT ON THE	
PROPERTIES OF ALUMINIUM DOPED ZINC OXIDE THIN FILMS	93
7.1 Introduction	93
7.2 Review of RF Magnetron Sputtered Aluminium Doped Zinc Oxide Thin Films	94
7.2.1 Introduction	94
7.2.2 Electrical Properties of Magnetron Sputtered AZO Thin Films	97
7.2.3 Structural Properties of Magnetron Sputtered AZO Thin Films	97
7.2.4 Optical Transmittance Properties of Magnetron Sputtered AZO Thin Films	3. 98
7.2.5 Summary	99
7.3 Experimental Details	100
7.4 Preliminary Experiment	101
7.5 Experiment 1	105
7.5.1 Introduction	105
7.5.2 Optical Transmission Measurements	106
7.5.3 Electrical Measurements	107
7.5.4 Grazing Incidence X-ray Diffraction Measurements	109
7.5.5 Atomic Force Microscopy and Scanning Electron Microscopy Analysis	111
7.5.6 X-ray Photoelectron Spectroscopy Analysis	112
7.6 Experiment 2	114
7.6.1 Introduction	114
7.6.2 Optical Transmission Measurements	115

7.6.3 Ellipsometry Fitting Analysis	116
7.6.4 Electrical Measurements	119
7.7 Conclusion	120
CHAPTER EIGHT: TRANSPARENT CONDUCTING ALUMINIUM DOPED ZINC	
OXIDE FOR SUPERSTRATE SILICON QD SOLAR CELL DEVICES	122
8.1 Introduction	122
8.2 Review of Current Silicon QD Solar Cell Device Designs	123
8.3 Experimental Details	131
8.3.1 Introduction	131
8.3.2 AZO Superstrate <i>n-i-p</i> Solar Cell Devices on Quartz	132
8.3.3 Superstrate AZO on B and P bilayers	135
8.4 Results and Discussion	138
8.4.1 Time-of-Flight Secondary Ion Mass Spectroscopy Analysis	138
8.4.2 Four-Point Probe Measurements	142
8.4.3 <i>I-V</i> Measurements	142
8.4.4 Suns-V <sub>oc</sub>	146
8.5 Conclusion	148
CHAPTER NINE: CONCLUSIONS, ORIGINAL CONTRIBUTIONS AND FUTURE	
WORK	149
9.1 Conclusions	149
9.2 Original Contributions to the Field and Their Significance	153
9.3 Scope for Future Work in the Field	154
9.3.1 Improvement to the Si NC Material Towards an Ideal Si QD Matrix	154
9.3.2 Improvements on the AZO Conductivity with Temperature and Better W	ays
to Utilise AZO with the Si NC Material	155
9.3.3 Si QD Solar Cell Devices in General	156
9.3.4 Other Areas of Research for Si QD Materials	158
LIST OF AUTHOR'S PUBLICATIONS	160
A. Journal Publications:	160
B. Conference Proceedings:	161
LIST OF TABLES	162

LIST OF FIGURES AND ILLUSTRATIONS
LIST OF SYMBOLS. ABBREVIATIONS AND NOMENCLATURE
A. Symbols and Physical Properties:
B. Materials and Devices:
C. Fabrication and Characterisation Techniques:
D. Miscellaneous:
FULL REFERENCE LIST 177

Epigraph

"I am enough of an artist to draw freely upon my imagination. Imagination is more important than knowledge. For knowledge is limited, whereas imagination embraces the entire world, stimulating progress, giving birth to evolution."

– Albert Einstein

# Chapter One: Introduction, Motivation, Aims and Objectives

## **1.1 Third Generation Photovoltaics**

Photovoltaics is the process by which solar radiation is converted to electrical energy through the use of semiconductor materials. Conventional first generation single-junction silicon solar cells are bound by the theoretical Shockley-Queisser limit of efficiency which is 31% at 1-sun and 40.8% at maximum terrestrial concentration [1] (1961). To exceed these limits, other approaches must be used and this is where third generation photovoltaics comes in. Third generation photovoltaics [2-4] aim to achieve higher efficiencies with low fabrication/production costs. The idea is to utilise second generation thin-film solar cell [5] deposition techniques with the use of materials that are non-toxic, abundant and robust.



**Figure 1.1.** Efficiency & cost projections of 1<sup>st</sup> (I), 2<sup>nd</sup> (II) and 3<sup>rd</sup> (III) generation PV technologies [2] (2003).

Figure 1.1 shows the three generations and their theorised efficiency to dollar per Watt price bubble in 2003. It was understood quite early on that traditional first generation wafer based crystalline Si (c-Si) solar cells have high per unit area manufacturing costs and

somewhat reasonable efficiencies. According to the latest International Technology Roadmap for Photovoltaics (ITRPV) the average price for multi-crystalline silicon (mc-Si) modules were 0.62 US\$/Wp in 02/2015 [6], with about 51% coming from the cell material and manufacturing cost and 49% from just the module manufacturing cost. This average price is actually surprisingly lower than what was predicted from the chart in Figure 1.1 in 2003. From the ITRPV the average stabilised efficiency for Si solar cells of all technologies on the market in 2015 was estimated to be between 18.2 to 23.0% and is estimated to increase to 26% in 2025 [6]. However, 26% is seen at the practical limit of efficiency for single-junction c-Si solar cells in production [7] as it impinges on the theoretical limiting efficiency of single-junction c-Si solar cells which is 29.43% [8]. This means that cost effectiveness may become an issue at some point in the future. The fundamental reason is that even under large manufacturing scales, the raw material costs become the limiting factor, hence the idea of second generation photovoltaics. Third generation concepts aim to increase the efficiency whilst reducing the material cost per unit area and ultimately reduce the whole balance-of-systems cost.



**Figure 1.2.** Energy band diagram displaying the main energy loss mechanisms: 1) nonabsorption due to photons with insufficient energy (i.e. energy below the bandgap); 2) thermalisation of photogenerated carriers; 3-4) contact and junction losses; 5) recombination loss [2].

Figure 1.2 shows the basic single p-n junction band diagram under illumination. To surpass the Shockley-Queisser limit, one must understand the fundamental energy loss mechanisms of conventional single-junction solar cells. Of the loss mechanisms shown, the largest losses for single-junction solar cells are 1) the inability to absorb photons with

wavelengths below the bandgap and 2) thermalisation of photons with energy greater than the bandgap. There are several ways to avoid these losses, which are:

- Multiple energy threshold processes, i.e. to increase the number of bandgaps by using multiple cells and there are several methods of achieving this such as spectrum splitting and tandem cells.
- 2) Having multiple carrier generation with either a high energy photon or the addition of two or more lower-energy photons.
- 3) The capturing of carriers before they thermalise, i.e. hot-carrier solar cells [9-11]).

Of the three advanced concepts only 1) has surpassed the Shockley-Queisser limit in practice. A brief discussion of multiple energy threshold concepts will be discussed below with progression towards all-Si nanostructure tandem solar cells.



**Figure 1.3.** Multiple bandgap concepts: (a) spectrum splitting; (b) tandem cell [4]. A combination of both concepts is also feasible.

Multiple bandgap concepts are shown in Figure 1.3. The concept of using light splitting to reach high PV efficiencies was first proposed by Jackson [12] in 1955. The spectrum splitting design, concept (a) in Figure 1.3, consists of complex spectrally sensitive mirrors and/or dichroic filters with multiple types of solar cells. This concept has been demonstrated with high efficiencies over the years in research [13-16]. However, the more

successful approach has been concept (b), the multi-junction or interchangeably the tandem solar cell approach. III-V tandem solar cells have already been demonstrated and widely used in concentrator photovoltaics [17]. Tandem solar cells essentially consist of multiple layers of different bandgap solar cells stacked on top of each other with the highest bandgap at the top (where light enters the cell) and the lowest at the bottom. This allows preferential absorption of the light in its various layers. There are two types of tandem cells: the "mechanically" stacked type with individual contacts for each of the subcells and the other type is the "monolithic" structure with the sub-cells connected in series with only two terminals for the whole stack. Factors such as correct bandgap combinations, layer thicknesses, lattice matching characteristics, doping and junction depth are all very important in the design of tandem cells and particularly the monolithic type. Over the years, the monolithic approach based on III-V materials has been more successful due to its simpler and more efficient two-terminal design. Only one substrate is needed in monolithic tandems which gives it a cost benefit over mechanically stacked tandem cells. However, the biggest disadvantages with III-V tandem solar cells compared to conventional c-Si solar cells are their high material cost, expensive growth techniques and the need for current matching in each of the sub-cells. High-quality III-V tandem cells require metalorganic vapour phase epitaxy (MOVPE) to achieve lattice matched singlecrystal arrangements. An alternative approach in terms of decreasing the \$/Watt and greater industrial scale manufacturability is to use alternative materials that are less costly and require lower energy deposition techniques. This brings the topic to all-Si nanostructure tandem solar cell research which is the main topic in this thesis.

# 1.2 All-Si Tandem Solar Cells

Nanostructures are an ever growing area in the optoelectronics and semiconductor industry. Research and development in this area seems to be intensifying with promising results. For solar cell applications, Si nanostructures can be bandgap engineered through the concept of quantum confinement either in one dimension as "quantum wells" (QW) or all three dimensions as "quantum dots" (QD<sup>\*</sup>). A tandem solar cell which is based only on Si elements and its dielectric compounds (consisting of common elements such as oxygen, nitrogen and carbon) can ultimately be produced by thin film deposition

<sup>&</sup>lt;sup>\*</sup> A Si quantum dot (QD) refers specifically to a Si nanocrystal (NC) that is spherical in shape with a diameter less than 10 nm. In this thesis, the terms Si QD and Si NC are used interchangeably.

techniques followed by some form of crystallisation via thermal annealing processes. The main advantage compared to III-V tandems is the abundance and non-toxicity of the materials used. Nevertheless these thin film deposition methods do come at a disadvantage due to poorer crystal quality with extensive defect densities and thus lower achievable efficiencies compared to III-V solar cells. Furthermore, these tandem cells need to be made thin to reduce recombination with short diffusion distances, thus high absorption coefficients are required [18].



Figure 1.4. A theoretical design of an all-Si tandem cell using quantum confined QDs [19].

The most important aspect for tandem solar cells is the value of the bandgaps of the individual sub-cells in the stack and depending on the type of reference spectrum the optimal combinations can be easily found. For example using the Shockley-Queisser detailed balance calculations [1] and the program code EtaOpt [20], a three-junction device with bulk silicon as the substrate would have 2.0, 1.5 and 1.1 eV as the ideal bandgaps (Figure 1.4) based on current matching for the AM1.5 spectrum. The whole idea of quantum confinement is that the bandgap of the materials can be engineered with precision to allow for the best possible combination such that the correct wavelength range of the incoming spectrum can be absorbed preferentially from top down and allow for better utilisation of the energy available, i.e. reducing losses 1 and 2 from Figure 1.1.

Despite the promising future of all-Si nanostructure tandem solar cells, the current photovoltaic quality of the Si QD material for the upper sub-cells is still very far from ideal. Consequently current research is still focused on improving the quality of the Si QD material and single-junction Si QD solar cell devices.

# **1.3 Thesis Objectives**

The thesis objectives are:

- To investigate the growth and nucleation kinetics of Si nanocrystals (NCs) in a SiO<sub>2</sub> matrix using *in situ* high resolution transmission electron microscopy with real time heating.
- To investigate and characterise the properties of high Si content silicon rich oxide (SRO)/SiO<sub>2</sub> bilayer superlattice thin film material with boron and phosphorus doping and address their advantages for Si QD photovoltaics.
- 3) To investigate the properties of magnetron sputtered transparent conducting aluminium doped zinc oxide (AZO) after thermal annealing up to 1100 °C.
- To demonstrate the first stand-alone superstrate configured Si QD solar cell device using AZO as a transparent conducting contact.
- 5) To investigate the contact between AZO and the high Si content B and P doped SRO/SiO<sub>2</sub> bilayer superlattice thin films.

# **1.4 Thesis Chapter Outline**

This chapter (Chapter 1) puts the rest of the thesis in context by briefly introducing third generation photovoltaics and motivation towards all-Si tandem solar cell research. The thesis objectives are also presented followed by this thesis chapter outline.

Chapter 2 and Chapter 3 are the literature review chapters. The literature review is separated into two chapters because it consists of two different topics. Chapter 2 outlines

the fundamental physical theory of silicon QDs and provides an overview of the experimental progress to date. The literature review in Chapter 2 serves as the underlying theory for the experimental Chapters 5, 6 and 8.

Chapter 3 reviews the literature on AZO and its use as a transparent conducting oxide (TCO). This chapter begins with a general background of TCOs, followed by properties of zinc oxide. The literature review in Chapter 3 serves as the theory for the experimental Chapters 7 and 8.

Chapter 4 presents the different fabrication, materials characterisation and photovoltaic device characterisation techniques used in the rest of the thesis. Some techniques include magnetron sputtering, furnace annealing, transmission electron microscopy, X-ray diffraction and Hall effect measurements. A brief introduction is given for each of the techniques followed by their purpose and relevance to the research work.

Chapter 5 is the first of the four experimental chapters. This experiment involves *in situ* high resolution transmission electron microscopy (HRTEM) observation of silicon NC nucleation in a  $SiO_2$  bilayered matrix. The purpose of this experiment is to study the solid-state nucleation and formation of Si NCs from SRO/SiO<sub>2</sub> bilayer superlattice samples using a special type of HRTEM equipped with a heating stage.

Chapter 6 is the second experimental chapter which studies the properties of high Si content SRO/SiO<sub>2</sub> bilayer superlattice thin films by various characterisation techniques. The dependence of annealing temperature on Si NC formation using both GIXRD and Raman spectroscopy is investigated as well as the effects of boron and phosphorus doping in the SRO layers.

Chapter 7 is the third experimental chapter which studies the properties of magnetron sputtered AZO thin films and their dependence on post annealing temperatures up to 1100 °C. A short literature review survey of magnetron sputtered AZO thin films is presented at the beginning of the chapter. A special method was discovered during the course of the experiments which allowed the AZO to partially retain of its conductive nature even after annealing at high temperature. This special method was used to create the superstrate Si QD solar cell devices in Chapter 8.

Chapter 8 is the final experimental chapter which combines the results from Chapter 6 and Chapter 7 to demonstrate for the first time the concept of a stand-alone superstrate Si QD solar cell device on quartz using AZO as the transparent conducting contact. This device is compared to the different Si QD devices designed by other authors in the past. AZO on B and P doped Si NC bilayers were also fabricated to examine the contact properties. New potential Si NC solar cell device structures are also discussed at the end of the chapter.

Finally Chapter 9 summarises the research work of this thesis. A list of unique contributions to the field of photovoltaics is also included. Lastly the chapter suggests directions for future work.

# Chapter Two: Basic Theory of Silicon Quantum Dots and Work to Date

# 2.1 Introduction

Quantum dots (QDs) are nanocrystals (NCs) made from semiconductor materials ranging in size from approximately 2-10 nm. As QDs are usually in the scale of a few nanometres, they are small enough to exhibit quantum mechanical properties. Their optoelectronic properties exist somewhere between bulk semiconductors and discrete atoms. QDs have possible applications in multiple areas from transistors, light emitting diodes (LEDs), diode lasers, medical imaging, quantum computing and solar cells. Research efforts in Si nanostructures and QDs have been focused in the areas of optoelectronics [21-26], semiconductor memories [27-31] and third generation photovoltaics [18, 19, 32-34]. In general terms, QD characteristics are related to the size and shape of their individual NCs, whereby the smaller the size the larger the bandgap and hence the greater the difference in the energy between the valence and conduction bands. The usefulness of QDs lies in this particular characteristic of bandgap tunability or bandgap engineering by simply varying their size or shape.

This chapter outlines the fundamental theory of Si QDs and provides an overview of the experimental progress to date in this field of research. As this thesis is mainly focused on the experimental side of Si QD solar cells the theory is not extensive and is simply here to serve as a brief overview for the reader. For more information on the theory, please refer to the references cited in this chapter.

# 2.2 Quantum Confinement in Si QD Nanostructures

In bulk semiconductors excitons are free to move in all directions, however when the dimensions of the semiconductor are reduced to the same order of magnitude as the characteristic length termed the "exciton Bohr radius", quantum confinement occurs. In other words, quantum confinement is the phenomenon where electrons and holes are squeezed into a dimension that approaches a critical quantum measurement and

consequently properties are modified because no two nearby electrons can share the same energy level according to Pauli's exclusion principle. Quantum confinement defines both the electronic properties (the arrangement of the energy levels in the semiconductor) and the optical properties. Often quantum confinement can be modelled using the "particle in a box" analogy which leads to the result that energy levels of QDs are related to their size and shape. As the dimensions of a QD approach the length of the exciton Bohr radius, electron crowding causes splitting of the original discrete energy levels into further smaller ones. Depending on the dimensions of confinement, three kinds of structures can be defined:

- 1) Quantum well (QW) confinement in one spatial dimension
- 2) Quantum wire (QR) confinement in two spatial dimensions
- 3) Quantum dot (QD) confinement in all three spatial dimensions.

The explanation below, adapted from Ref. [35], shows how the effective mass approximation (EMA) can be used to determine the absolute confined energy levels for such small NCs. As with most approximations, there are limitations and deviations from the true nature of these nanostructures. The EMA of the solution to the Schrödinger equation for electrons (or holes) confined in three dimensions for the increase in energy for the *n*th confined energy level in a QD is shown below:

$$\Delta E_n = \frac{\hbar^2 k^2}{2m^*} \tag{2.1}$$

where  $\hbar$  is the reduced Planck's constant  $\left(\hbar = \frac{h}{2\pi}\right)$ , *k* is the wave-vector and *m*<sup>\*</sup> is the effective mass of the particle.

For a QD with a diameter *a* is confined by an infinite or large potential barrier:

$$k\frac{a}{2} \approx n\pi \tag{2.2}$$

10

Hence, the confined energy level can be found by substituting Eq. (2.2) into Eq. (2.1) yielding the discrete solutions for quantum numbers in each confined dimension denoted by  $n_1$ ,  $n_2$  and  $n_3$ :

$$\Delta E_n = \frac{\pi^2 \hbar^2}{2m^* a^2} (n_1^2 + n_2^2 + n_3^2) = 3 \frac{\pi^2 \hbar^2}{2m^* a^2} n^2$$
(2.3)

Note:  $n_1 = n_2 = n_3$ .

The equation above is similar to the solution for a QW which is confined in one dimension and the extra ×3 term is due to the confinement in all three dimensions in the case of a QD. The corresponding energy levels for QWs and QDs are non-degenerate with the same quantum number, i.e. in Eq. (2.3),  $n = n_1 = n_2 = n_3$  and therefore for a specific size of confinement a QW has confined energy levels a third of the height of a QD. In physical terms, for a given quantum confinement level the size or diameter of a QD is  $\sqrt{3}$  of the width of a QW. Note this relation applies strictly only for a cubic quantum dot, whereas for a spherical QD of diameter, *d*, the confinement is actually a little greater with a factor that is slightly larger than  $\sqrt{3}$ . As mentioned before and as a reminder to the reader, the EMA predicts the general trend of an increase in confined energy level with the decrease in dimension of these quantum structures.

Given the symmetry of the conduction band valley and valence band hill leading to a 2-fold degeneracy in the transverse directions for Si the effective masses have been calculated [36] as  $m_e^* = 0.27m_0$  and  $m_h^* = 0.59m_0$  for electrons and holes respectively. By substituting the above approximate masses into Eq. (2.3) for the first quantised ground state energy yields:

$$E_1 = E_g + \Delta E_1 = E_g + \frac{4.1808}{a^2} + \frac{1.9132}{a^2} = E_g + \frac{6.09408}{a^2}$$
(2.4)

for a in nm and  $E_1$  and  $E_g$  (bandgap of bulk Si) in eV.

The results of the above equation show that there is an increase in bandgap energy with the decrease in the dimensions of the QD. This is because smaller QDs result in a more pronounced overlap or folding of the wave-function in k-space with transitions becoming more quasi-direct. This has been proven experimentally from photoluminescence (PL) data on QD nanostructures from various sources in Ref. [18]. However the EMA deviates progressively as the diameter of the QD decreases, this is partially due to the fact that experimentally, the confining barriers are non-infinite. In the case of real dielectric matrices, the approximation of k in Eq. (2.2) has to be calculated implicitly via:

$$k\frac{a}{2} = n\pi - \sin^{-1}\left(\frac{\hbar k}{\sqrt{2m^* V_0}}\right)$$
(2.5)

where  $V_0$  is the confining barrier height. Hence,  $\Delta E_n$  is reduced to [36]:

$$\Delta E_n \approx \frac{3 \cdot \frac{\pi^2 \hbar^2}{2m^* a^2}}{\left(1 + \frac{\hbar}{\left(\frac{a}{\sqrt{2m^* V_0}}\right)}\right)^2} \cdot n^2$$
(2.6)

For finite confinement barriers,  $\Delta E_n$  from Eq (2.6) will also be lower than Eq. (2.2). Thus, finite confinement barriers will lower the confinement energy.

# 2.3 Carrier Tunnelling Transport in Si QD Superlattices

Carrier transport properties are dependent on the type of matrix that Si QDs are embedded in. Figure 2.1 shows three different matrices that Si QDs may be confined in. It is shown that each type has different transport barriers with tunnelling probabilities closely related to the barrier height. SiO<sub>2</sub> (bandgap 9eV) has the highest barrier, followed by Si<sub>3</sub>N<sub>4</sub> (bandgap 5.3 eV) and SiC (bandgap 2.5 eV), with the lowest barrier. This means that compared to Si QDs in SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub> or SiC can have greater spacing between each other for a given tunnelling current value.



**Figure 2.1.** Bulk band alignments between crystalline Si (c-Si) and its corresponding oxides (SiO<sub>2</sub>), nitrides (Si<sub>3</sub>N<sub>4</sub>) and carbides (SiC) [18].

It is known that the wave-function, k, of an electron confined to a spherical QD influences the surrounding material which decreases in an exponential fashion into the barrier. Also, the rate of the exponential decay is reduced for a lower barrier height material. The approximate equation for tunnelling probability,  $T_e$  through a "square" potential well is shown below [36]:

$$T_e = 16e^{\left(-d\sqrt{\frac{8m^*}{\hbar^2}\Delta E}\right)}$$
(2.7)

where, *d* is the barrier width or separation between the QDs,  $m^*$  is the effective mass of the electron within the barrier,  $\sqrt{\Delta E} = \sqrt{E_C - E_V}$ , the square root of the energy difference between the conduction band edge of the matrix to the confined energy level of the QDs as viewed by the electron and  $\hbar$  is the reduced Planck's constant. By combining the first three parameters, the tunnelling probably of QDs will be dependent on the factor  $m^*d^2\Delta E$ . This means in qualitative terms that for a given tunnelling probability, if the barrier height is increased then the barrier width, i.e. separation between the QDs, should decrease and vice versa. Furthermore, as the size of the QD decreases (higher bandgap)  $\Delta E$  will decrease, which would give a higher tunnelling probability. Note, that Eq. (2.7) only assumes the ideal case where electrons are tunnelling between two isolated QDs and hence should be used merely as a qualitative outlook. In reality, the tunnelling probability will depend on the coupling of wave-functions across many QDs.

Jiang and Green [37], used the effective mass approach shown above to calculate the conduction band structure of three-dimensional cubic Si QD superlattices embedded in matrices of SiC,  $Si_3N_4$  and  $SiO_2$ . They first showed that the calculated band energy is not highly sensitive to a change in the dielectric effective mass of the electron compared to the QD size and distribution. However, it was found that the interdot separation has a larger influence on the "Bloch" carrier mobilities than the actual size of the QDs.

In summary, to theoretically increase the tunnelling probability and hence mobility of QD materials, the effective mass of the electrons in the barrier would need to be as large as possible (smallest effect), the size of the QDs to be as small as possible, the height of the confining matrix barrier material to be as low as possible and the separation in the QDs as small as possible (largest effect). In terms of the confining matrix barrier material, theory postulates that SiC with a bandgap of 2.5 eV would be the best candidate for Si QD solar cells. However in reality, as the polarity and the length of the Si-Si bonds decrease from SiO<sub>2</sub> to Si<sub>3</sub>N<sub>4</sub> to SiC, the phase segregation and nucleation of Si in SiC matrices would also be the least effective of the three types of matrix material.

# 2.4 Fabrication of Si QD Nanostructures and the SRO/SiO<sub>2</sub> Superlattice Structure

Si NCs, which exhibited room temperature (RT) PL, were fabricated by sputtering Si into  $SiO_2$  as early as 1988 [38]. In the following years other techniques included ion implantation of Si into  $SiO_2$  matrices followed by thermally induced crystallisation of the Si [39-41]; etching of porous Si [22, 42]; CVD [43-45], reactive evaporation [46] and sputtering [47-50] of sub-stoichiometric  $SiO_x$  (where 0 < x < 2) films followed by thermal annealing/nucleation. The main problem with these methods is the broad size distribution of the resulting non-constrained Si NCs which makes characterisation more complicated and the material less useful for making practical devices. Some form of confinement must then be used to decrease the size distribution of these Si NC films. The first attempt at confining these Si NCs was the amorphous Si (a-Si)/SiO<sub>2</sub> superlattice structure by Lu *et al.* 

[23] back in 1995. There were further improvements to this design by incorporation of a post high temperature anneal [51, 52]. However there was a major drawback to this method as the NCs fabricated in this way could not be constrained in all three directions due to the thickness of the Si layer that was used. Another problem with the method used was the resulting layered structure was more of a polycrystalline film due to the NCs touching each other. A large size distribution of the Si NCs still made the PL spectrum broad. In 2001, Zacharias et al. presented a neat and simple method of constructing Si QDs that were constrained satisfactorily in all three directions [53]. The fundamental technique involved deposition of alternating bilayers of stoichiometric silicon rich oxide,  $SRO^{\dagger}$  (or SiO<sub>x</sub> used interchangeably) and silicon dioxide, SiO<sub>2</sub>, which forces the NCs into a "dense and layered arrangement" [53]. Once this step was complete a post-deposition thermal anneal was then required to nucleate the Si QDs (Figure 2.2). In the study by Zacharias et al., the SiO<sub>2</sub> dielectric barrier layers were 2 nm or 3 nm and the SRO layer with a silicon-to-oxygen ratio of 1:1 was either 3 nm or 1 nm. The samples consisted of 46 to 96 bilayers which were later annealed at 1100 °C for 1 hour in a nitrogen ( $N_2$ ) atmosphere. Through this method Zacharias et al. claim that precise size and control of density of the Si NCs can be managed independent of the stoichiometry.



**Figure 2.2.** Superlattice bilayered structure illustrating the nucleation of Si QDs in a "Silicon Rich Oxide" (SRO or SiOx) layer [18].

For most semiconductor device applications, precise engineering of spatial position, size, shape and the density of these NCs is critical. Thin film deposition techniques are required

<sup>&</sup>lt;sup>†</sup> Silicon rich oxide in this thesis is abbreviated as SRO or  $SiO_x$ . SRO is normally used in general, whereas  $SiO_x$  is used when the stoichiometry is emphasised.
for nanostructure fabrication. The most common thin film deposition techniques used to fabricate these Si based superlattices are plasma enhanced chemical vapour deposition (PECVD) and sputtering. Both of these deposition techniques are well established and have advantages over other techniques such as: low temperature deposition, large availability of different deposition materials, good uniformity over a large area, precise deposition rate and many others.

For the case of Si QDs embedded in a SiO<sub>2</sub> matrix, the phase separation of excess Si in the SRO layers by a high temperature anneal (usually between 1050-1150 °C in N<sub>2</sub>) is governed by the following equation:

$$SiO_x \rightarrow \frac{x}{2}SiO_2 + \left(1 + \frac{x}{2}\right)Si$$
 (2.8)

where 0 < x < 2 [53]. The phase separation of the SiO<sub>x</sub> ensures that nucleated Si NCs will be separated from one another via SiO<sub>2</sub> shells. Furthermore, Zacharias *et al.* with the aid of cross-sectional transmission electron microscopy (TEM) showed that the selfarrangement of the Si NCs is destroyed if the buffer SiO<sub>2</sub> layer is too thin, specifically below 2 nm thickness; this is due to the interaction with the interface roughness or in the other case if the layer is too thick then strain relaxation occurs. With regard to the size of the Si QDs themselves, the lower limit is set by the crystallisation theory adapted to fit nanometre-thick layers [54] and this turns out to be approximately 1.8 nm for the type of superlattice structure presented above. Definitive PL characterisation showed a strong blue-shift with decreasing NC size (Figure 2.3).



**Figure 2.3.** Normalised PL spectra displaying a definitive blue-shift concurrent with the NC diameter [53].

Zacharias *et al.* presented a simple method in constructing these Si QD nanostructures with good control of both size and density. PL and TEM characterisation were performed on the samples with positive although limited results. Further investigation is required in terms of the structure of the NCs. Some authors [55-59] through various TEM techniques have reported elliptical or more extensive networks deviating from the expected spherical QD shape. This is more likely to occur for relatively thick layers where diffusion is not constrained. Potential merging of several QDs is also a possibility. The irregular shape will most certainly affect the quantum confinement of excitons due to their higher interface defect densities as the surface area-to-volume ratio increases when the shape digresses from that of an ideal spherical QD, at least for QD with the same amount of Si atoms. Also, the uniformity of QDs and methods to decrease the size distribution even with this superlattice structure should be improved. Both these issues will most certainly affect the material. In addition electrical characterisation such as conductivity and electron or hole mobility should be further explored.

## 2.5 Effect of Silicon Rich Oxide Stoichiometry on the Properties of Si QD Superlattice Structures and the Size and Density Control of Si QDs

To date, the most extensive investigation has been with Si QDs embedded in a SiO<sub>2</sub> matrix. Hao *et al.* [60] investigated the structural and optical properties when the stoichiometry of the SRO is altered. Their experiment involved co-sputtering multiple bilayers of SRO/SiO<sub>2</sub> films on Si wafers and quartz substrates followed by a thermal anneal at 1100 °C for 1 hour in a N<sub>2</sub> atmosphere. The method used was similar to the one outlined in the previous section. The O/Si ratio in the SiO<sub>x</sub> was the dependent variable in their experiment with *x* being 0.86, 1.0 and 1.3. The thicknesses of the SRO and SiO<sub>2</sub> layers were approximately 4 nm and 6 nm respectively. Each superlattice sample consisted of fifteen bilayers with approximate stoichiometry denoted as SiO<sub>0.86</sub>/SiO<sub>2</sub>, SiO<sub>1.00</sub>/SiO<sub>2</sub> and SiO<sub>1.30</sub>/SiO<sub>2</sub>.

TEM measurements were performed on the samples which showed clear multi-layer formation and at higher resolution clear QD structures could be seen (Figure 2.4). As expected the TEM images showed that the average QD size decreases as the O/Si ratio increases from 0.86 to 1.30 and the total number and density of the QDs also decreases. Both these observations were consistent with similar work from Yi *et al.* [61]. Hao *et al.* also show together with GIXRD that the average size of the Si QDs is smaller in a multilayered structure versus an unconstrained full monolayer structure, i.e. Si QDs embedded in a thick a-SiO<sub>2</sub> layer. In addition, from other sources, the size distribution of the Si NCs is greater in an unconstrained full monolayer structure [61, 62].



**Figure 2.4.** TEM images of cross-sectional annealed SRO/SiO<sub>2</sub> specimens: (a)  $SiO_{1.30}/SiO_2$  multiple bilayers (b)  $SiO_{1.30}/SiO_2$  multiple bilayers at higher magnification (c)  $SiO_{1.00}/SiO_2$  multiple bilayers (d)  $SiO_{1.00}/SiO_2$  multiple bilayers at higher magnification (e)  $SiO_{0.86}/SiO_2$  multiple bilayers (f)  $SiO_{0.86}/SiO_2$  multiple bilayers at higher magnification [60].

Hao *et al.* also investigated the optical properties on the O/Si variation in the multi-layered films. Their conclusions were that the optical absorption is blue-shifted with an increase in the O/Si ratio as bandgap becomes larger when the size of the QD decreases. Also, as the O/Si ratio decreases, i.e. as x increases, the degree of absorption increases. This is intuitive as an increase in Si content in the SRO layers with the same thickness means that there is more Si to absorb the incoming photons. This does not necessarily mean that

the absorption coefficient is higher for SRO layers with a lower O/Si ratio, only that there are more QDs for the absorption. It is experimentally difficult to compare the absorption coefficients in this way, as it is still not possible to fabricate superlattices with different size QDs whilst having the same QD population density. In reality, quantum confinement theory would dictate that smaller Si QDs would have a higher absorption coefficient due to the loss of their indirect bandgap nature with the decrease in dimension. Further discussion on the direct versus indirect bandgap of Si QDs can be found in *"Silicon quantum dot based solar cells: addressing the issues of doping, voltage and current transport"* by Conibeer *et al.* [63].

It was also reported that the PL spectrum changes with the O/Si ratio in band position, FWHM and intensity. It is important to mention that the correct inference of the optical data is difficult and limited. It should be interpreted with care due to the fact that the change in the O/Si ratio may not only change the QD size, but also their size distribution and concentration, type of phase (crystalline or amorphous) and/or QD surface properties  $(Si/SiO_2 \text{ or } Si/SiO_x \text{ interface [64]})$ . The tolerance to the thickness of the layers also plays a part in the optical data analysis [61]. From the PL measurements there was a clear redshift from SiO<sub>1.30</sub>/SiO<sub>2</sub> to SiO<sub>1.00</sub>/SiO<sub>2</sub> which follows the quantum confinement theory and was consistent with the work of several authors [53, 61]. However from  $SiO_{1.00}/SiO_2$  to SiO<sub>0.86</sub>/SiO<sub>2</sub> there was another blue-shift which is the opposite of what quantum confinement theory posits. The explanation for this is that different properties and mechanisms come into play besides just QD size, for example the different types of phase (crystalline or amorphous) or QD surface properties. It is possible, given the higher Si content in the SiO<sub>0.86</sub>/SiO<sub>2</sub> multi-layers, that there is the existence of weakly absorbing background a-Si atoms or sub-stoichiometric SiO<sub>x</sub> causing the blue-shift. A more comprehensive explanation is given by Hao et al. [60] and Allan et al. [65].

Elsewhere, Yi *el al.* [61] performed some similar experiments using reactive evaporation to fabricate the  $SiO_x/SiO_2$  superlattices. In their experiment they kept the stoichiometry of the SRO layers constant whilst varying the thickness of the SRO layers from 2 to 7 nm. Most importantly, they demonstrated that the size of the Si QD could be well controlled by varying the SRO up to a thickness of **5 nm** (which is around the exciton Bohr radius of bulk Si). However, after 5 nm, more than one NC nucleus could form over the total layer thickness.

### 2.6 Doping of Si QD Nanostructures

Impurity doping of Si NCs is more complex than doping in c-Si as impurity doping can drastically alter the structural, electrical and optical properties of the Si NCs themselves. Boron (B) and phosphorus (P) are the most common dopants for c-Si solar cells. Assuming that bulk c-Si has a density of  $5 \times 10^{22}$  atoms/cm<sup>3</sup> or approximately 50 atoms/cm<sup>3</sup>, the number of Si atoms in typical Si QDs with a diameter of 3 nm and 5 nm will be approximately 700 and 3300 respectively. A simple matrix model consisting of 5 nm cubic Si QDs separated by 2 nm of SiO<sub>2</sub> with 1 dopant atom per QD would translate to a bulk doping density of about  $3 \times 10^{18}$  cm<sup>-3</sup>. It was found however that dopant densities used to dope Si QDs in the SRO/SiO<sub>2</sub> superlattice structures are actually much higher as a large number of dopants are in fact inactive and do not contribute to the doping. Previous *ab initio* studies have shown that the formation energy for doping of Si NCs is higher than bulk c-Si mainly because of the reduced dimensionality [66]. Furthermore the formation energy of the dopant increases with decreasing Si NCs size (Figure 2.5).



**Figure 2.5.** Formation energy of dopant atoms of (a) B and (b) P placed substitutionally at the centre of a Si nanocluster as a function of inverse NC radius. The shapes (filled square, empty square and empty triangle) represent different modelling regimes [66].

Figure 2.5 shows the modelled formation energy of (a) B and (b) P dopant atoms placed substitutionally at the very centre of a Si nanocluster as a function of the inverse radius of the Si nanocluster. The shapes in the graphs represent different modelling regimes (for more information please refer to Ref. [66]). Cantele *et al.* [66] point out that for a particular nanocluster radius, R, the bond relaxation surrounding the central dopant causes a reduction in the formation energy. However, the overall effect is small compared to the dependence on the radius of the nanocluster. This effect of increasing size (due to increasing annealing temperature) on the doping efficiency of Si NCs has been shown experimentally by Fujii *et al.* [67] through PL measurements of Si NCs embedded in SiO<sub>2</sub> which were individually doped by B and P.

Furthermore, Cantele *et al.* show through their *ab initio* study that the position of the dopant impurity within the NC also has a strong effect on the formation energy. In Figure 2.6, the effect of location on the formation energy of B in a Si<sub>146</sub>BH<sub>100</sub> nanocluster is presented. In short, as the B dopant is moved towards the surface of a Si NC, the formation energy decreases. This assumption is plausible due to the fact that such positions may allow greater atomic bond relaxation around the impurity. The conclusion then seems to be that the sub-surface positions are more stable and energetically favourable. Further evidence is provided through the "self-purification" mechanism [68] in Si QDs.



**Figure 2.6.** (a) Location of the dopant impurity within the Si nanocluster as it moves along two separate paths to the surface (b) The formation energy of the dopant impurity versus the distance from the central location (marked by the numbers 1-6) [66].

Despite the theoretical difficulties, "successful" doping of Si NCs has been demonstrated by several reports [63, 67, 69-73]. Specifically Hao *et al.* has demonstrated doping of Si QDs in SRO/SiO<sub>2</sub> superlattices by co-sputtering of B for *p*-type and phosphorus pentoxide ( $P_2O_5$ ) for *n*-type samples. XPS measurements showed the existence of B-B/B-Si [70] and P-P/P-Si [74] bonding. In addition, XPS estimated that the atomic ratio of O/Si in the SRO layers was approximately 0.694 for the intrinsic (undoped) samples [71], with little change in the atomic ratio of O/Si for the doped samples. Transmission line measurements (TLM), a type of lateral resistivity measurement method proposed by Reeves and Harrison [75] were performed to evaluate the resistivity of the doped Si QD superlattices at 300K in the dark.



**Figure 2.7.** (a) Resistance versus B dopant concentration in 4 nm SRO/6 nm SiO<sub>2</sub> superlattices (15-bilayers) on quartz measured by TLM [63, 70]. (b) Resistance versus P dopant concentration in 5 nm SRO/6 nm SiO<sub>2</sub> superlattices (15-bilayers) on quartz measured by TLM [71].

Figure 2.7(a) shows that the intrinsic samples have a very high resistivity of  $1.0 \times 10^8 \Omega$ cm, but decreases by about two orders of magnitude to  $1.0 \times 10^6 \Omega$ cm when the B doping is increased to 0.17 atomic percent and decreases by another four orders of magnitude to  $1.0 \times 10^2 \Omega$ cm as the doping is further increased to 0.5 atomic percent. This decrease in resistivity gives a strong indication of effective doping in Si QDs as a consequence of increased carrier concentration. The situation is slightly different for P doping in Figure 2.7(b) however, because as the doping is increased from 0 to 0.1 atomic percent, the resistivity drops sharply by over seven orders of magnitude from  $1.3 \times 10^8$  to  $1.0 \times 10 \Omega$ cm. However from 0.1 to 0.35 atomic percent, the resistivity actually increases by just under three orders of magnitude to  $1.8 \times 10^3 \Omega$ cm. Possible reasons for this could be the over saturation of the Si QD surface states, clustering of P atoms and/or degradation of the Si crystallinity as a result of over doping. The result then implies that there is an optimum P doping level.

Elsewhere, metal oxide semiconductor (MOS) devices (pp. 197) [76] were fabricated by Dong *et al.* [77] to estimate the true doping density of B and P in SRO/SiO<sub>2</sub> superlattices structures via capacitance-voltage (C-V) measurements. The reported MOS structures consisted of 25 bilayers of 2 nm thick SiO<sub>2</sub> and 4 nm thick B or P doped SRO (with a Si-to $SiO_2$  ratio of approximately 1:1) followed by a 20 nm  $SiO_2$  as the oxide and AI as the metal contacts.

**Table 2.1.** Results of the material properties extracted by C-V measurements of B and Pdoped SRO/SiO2 superlattices in a MOS structure [77].

higher Si% samples	B doped	P doped
doping type doping concentration $(cm^{-3})$ oxide thickness (nm) surface charge density $(C cm^{-2})$ mobility <sup>a</sup> $(cm^2/V/s)$	$p \\ 4 \times 10^{17} \\ 12.5 \\ -1.6 \times 10^{12} \\ 2.2$	$n \\ 1 \times 10^{17} \\ 10.8 \\ 1.5 \times 10^{12} \\ 8.9$

<sup>a</sup>This is an effective mobility calculated from  $\mu = 1/qn\rho$ .

Table 2.1 shows the important material properties extracted by C-V measurements for B and P doped  $SRO/SiO_2$  superlattices in a MOS structure. Firstly, it should be noted that the method that the authors used to extract the mobility of their  $SRO/SiO_2$  material is different from that for c-Si. The conductance is dependent on both the separation between the QDs and the dopant concentration in the SRO layers. However it is difficult to separate these two dependencies. Nevertheless, they state that the mobility can still be estimated by the standard equation:

$$\mu = \frac{1}{qn\rho} \tag{2.9}$$

where *q* is the elementary electronic charge, *n* the doping concentration and *p* the resistivity. From Table 2.1, the effective/active doping densities for both the B and P doped SRO/SiO<sub>2</sub> superlattices are  $4 \times 10^{17}$  cm<sup>-3</sup> and  $1 \times 10^{17}$  cm<sup>-3</sup>, while the mobilities are 2.2 cm<sup>2</sup>/Vs and 8.9 cm<sup>2</sup>/Vs respectively. These mobility values are rather low compared to c-Si with the same active doping concentrations (if we assume the dopant concentration is  $1 \times 10^{18}$  cm<sup>-3</sup> then the mobility for B and P doping would be approximately 200 and 400 cm<sup>2</sup>/Vs respectively [78]).

Fundamentally, this is expected, as the dielectric matrix that the Si QDs are confined in is the insulator SiO<sub>2</sub> which in itself has a very high resistivity of roughly  $10^{17}$ - $10^{18}$  Ωcm [79]. As mentioned in the Section 2.3 "Carrier Tunnelling Transport in Si QD Superlattices", the mobility is strongly dependent on the interdot separation of the QDs as well as the size of the QDs. The carriers can only travel either through tunnelling across the dielectric barriers or "hopping" from one QD to another. Another effect on mobility is the high defect densities in the superlattice material itself, which usually increases with doping concentration especially when the majority of the dopants are not actually active. Importantly, Dong *et al.* mention that the extracted doping density and mobility do not correspond directly to that of the Si QDs, rather the material as a whole, which comprises all of the dielectric matrix, the interfaces and the quantum dots.

Contact properties of aluminium and nickel on the doped SRO/SiO<sub>2</sub> material were also investigated through TLM and it was found that the contacts were ohmic. This indicates that the films were either heavily doped or more likely that the surface defect density was very high. Furthermore, it was found that the contact resistivity decreased for films with higher Si contents.

## 2.7 Doping Characteristics of Silicon QD Superlattice Structures

As shown in the previous section, there is some evidence to show effective doping of SRO/SiO<sub>2</sub> films. However, the exact doping characteristics of the Si QDs are still not well understood. Theoretical work has shown that substitutional doping inside perfectly crystalline Si QDs is highly unlikely as it is energetically unfavourable for this to occur [66]. The mechanism of "self-purification" termed by Dalpian *et al.* [68], i.e. the segregation of the dopant atoms from within the perfectly crystalline NC to the surface seems to be the general consensus surround modelling work in this area [66, 69, 80]. Furthermore as the size of the NC decreases, the formation energies of defects increases meaning that it becomes even more difficult for impurities/dopants to exist inside smaller NCs [68]. Stegner *et al.* [69] show from experimental electron paramagnetic resonance (EPR) data on free electron density in P doped Si NC films that 95% of P atoms are in fact inactive and self-purified to the surface. For NC diameters above 12 nm in the EPR experiment the number of electrically active substitutional P atoms and hence the free donor-electron

density are at least one order of magnitude smaller than the number of total P atoms in their films. The authors further report that for smaller NC diameters with higher P densities, the free donor-electron density sharply decreases. They attribute this result to the "inter-NC compensation or electron capture at surface states". In conclusion they then state that control of doping in Si NCs is better and more well-defined the larger the size of the Si NC, namely greater than 12 nm in diameter [69].

A second possibility is doping of just the dielectric matrix material, i.e. the SiO<sub>2</sub> surrounding the Si QD. The idea is that the doped matrix can provide free carriers which can then be captured by the QD. This mechanism, usually known as "modulation doping" is often encountered in III-V semiconductor nanostructures. However, in III-V semiconductor nanostructures, the barrier height is typically in the order of a few 100 meV [36], which means that ionisation of dopant atoms is fairly probable at RT. However, in SRO/SiO<sub>2</sub> superlattices nanostructures, the dielectric matrix SiO<sub>2</sub> has a barrier height of 9 eV, making the ionisation of dopant atoms at RT highly improbable ruling out this possibility, shown in Figure 2.8(a). The "modulation doping" can only happen through direct tunnelling of carriers if the dopants in the SiO<sub>2</sub> are in the vicinity of less than 1 nm from the QDs which in reality is usually not the case.



**Figure 2.8.** Schematic illustration of two different mechanisms. (a) Doping of the dielectric a-SiO<sub>2</sub> material surround the Si QD with an abrupt transition. (b) Doping of the amorphous sub-oxide region surrounding the Si QD [32].

The third and most likely scenario is the doping of the stoichiometric sub-oxide (SiO<sub>x</sub>, where 0<x<2) region surrounding the QDs. Daldosso *et al.* [64] provide strong evidence of this through energy filtered transmission electron microscopy (EFTEM) and *ab initio* total energy calculations. They show through experimental and theoretical studies that the interface between the crystalline Si QDs and the surrounding dielectric SiO<sub>2</sub> matrix is not abrupt. A transition region, of amorphous nature, links the two together. This amorphous SiO<sub>x</sub> could provide flat "Bloch" bands doped in a pseudo bulk-like fashion. If the SiO<sub>x</sub> was highly Si rich, where *x* was less than 0.5, the shallow B and P doping levels would allow ionisation at RT as shown in Figure 2.8(b). The free donor-electrons or donor-holes can then be easily captured by the adjacent Si QDs and raise or lower the Fermi level in the material and result in *n*- or *p*-type material respectively. Direct doping of the sub-oxide itself is also a possibility.

The three scenarios suggested above are still subject to debate until further evidence on the exact position of dopant atoms is elucidated. Characterisation techniques such as atom probe tomography (APT), EPR, high resolution electron energy loss spectroscopy (HREELS), aberration corrected high resolution TEM (HRTEM) and/or energy-filtered TEM (EFTEM) may be needed to further analyse these Si QD superlattice materials.

### 2.8 Summary

Si QDs are a promising material for all-Si tandem solar cells due to their ability to vary their bandgap with size due to quantum confinement. They are promising candidates for upper sub-cells in tandem stacks with c-Si as the bottom sub-cell to improve on the Shockley-Queisser limit of efficiency for single-junction solar cells. However, the main issue is still with the Si QD material. More precise and comprehensive understanding of the structural, optical and electrical properties of Si QD material is still required. Special characterisation techniques such as various high resolution transmission electron microscopy techniques, atom probe tomography and photo-thermal deflection spectroscopy may also bring new insight to this area of research.

Addressing the quantum confinement involves shifting down to smaller QDs which would increase the bandgap of the material which is desired for upper sub-cells in a tandem solar cell for preferential absorption of "shorter" wavelength photons. Furthermore transport properties may be improved as a result of smaller QDs (see Section 2.3). The current problem here however is the need for tighter control, precision and repeatability in the deposition techniques as the dimensions are decreased. This is still extremely difficult in the present time as there are limitations in the precision of current deposition systems.

Finally, the current transport of both the Si QD material and photovoltaic devices need to be improved. Possible ways to do this include, decreasing the size distribution, maintaining the spherical shape and increasing the density of the Si QDs. A decrease in the size distribution of the Si QDs would see a reduction in the radiative recombination and improve uniformity of Si QDs in the layers due to better current transport. By maintaining the spherical shape, the surface area to volume ratio of the QD would be at a minimum which should theoretically result in the lowest amount of surface defects. A better method would be to increase the density of the Si QDs which would increase the absorption cross-

section to allow more photons to be absorbed in a per-volume basis. The higher density would also improve the mobility and current transport as the inter-dot distance is decreased thus improving the tunnelling and "hopping" probabilities (see Section 2.3). Also, although not explored in this thesis, using a dielectric material with a lower barrier height should theoretically improve the current transport. Finally, a better device architecture, such as using a conducting substrate or transparent conducting oxide (common in thin-film photovoltaics), would aim to reduce lateral current flow and improve current transport (Chapter 8).

# Chapter Three: Properties of Transparent Conducting Aluminium Doped Zinc Oxide

### 3.1 General Overview of Transparent Conducting Oxides

Transparent conducting (or conductive) oxides (TCOs) are a unique type of material with high optical transparency and good electrical conductivity. In photovoltaics, TCO thin films act as a window layer for light to pass through to the active material underneath for carrier generation as well as a means to transport current out of the photovoltaic device. TCOs have bandgaps which are usually larger than 3.2 eV that allow photons in the visible (390-700 nm) and some photons in the near infrared (800-2500 nm) spectral region to be transmitted. The most common TCOs for photovoltaics are tin doped indium oxide ( $In_2O_3$ :Sn) which is abbreviated as ITO [81-83]; fluorine doped tin oxide (SnO<sub>2</sub>:F) as FTO [84, 85] and various dopants for zinc oxide [86-91]. Currently, ITO has the best properties in terms of transparency and conductivity compared to FTO or doped ZnO, however it is not the best option for long term large scale manufacturing due to the low abundance of indium.

TCOs are essential for thin-film photovoltaics because they provide a way to extract the photocurrent. TCOs reduce the series resistance by providing a lateral conducting pathway for current which is illustrated in Figure 3.1. In a-Si solar cells for example, the intrinsic a-Si active material has a fairly high resistivity of around  $3 \times 10^5 \Omega$ cm [92], so carriers must first travel vertically to the TCO before they can be collected by the metal contacts or fingers. The lateral distance that carriers have to travel in the doped ZnO can be fairly large; this is to allow a sufficient area to receive sunlight; therefore the resistivity of the doped ZnO must be low. If there was no TCO, but only metal fingers, a significant amount of current would be lost due to the series resistance resulting in a heavy efficiency loss. This is not the case however for first-generation Si wafer based solar cells where metal fingers directly contact the relatively thick and doped emitter to provide sufficiently low sheet resistance typically in the 30-100  $\Omega/\Box$  range [93]. This minimises the series resistance to a level that would not significantly lower the efficiency of the wafer based solar cell. However with thin-film solar cells this is not possible.



**Figure 3.1.** Schematic diagram of a typical amorphous silicon (a-Si) solar cell illustrating the necessity of TCOs for thin-film solar cells. Typical values for the thicknesses are given for each layer.

The important criteria that make an effective TCO for thin-film solar cells are as follows:

- High transmittance in the visible and near infrared spectrum
- High conductivity (<  $10^{-3} \Omega cm$ )
- Good interface to the underlying active semiconductor/absorber material
- Must be able to be deposited uniformly over large areas via a type of thin film deposition method

Doped ZnO, over **all** other TCOs, satisfies the above criteria as well as one more important criterion, namely the ability to withstand elevated temperatures above 1100 °C (an important fabrication step in solid-state nucleated Si QD solar cells for this thesis). The next section examines the structural, electrical and optical properties of ZnO in closer detail with emphasis on its use as a TCO thin film.

### 3.2 Introduction to Zinc Oxide

#### 3.2.1 A Brief History and Applications of ZnO

Zinc oxide is an inorganic compound widely used in the electronics industry for ferrites, phosphors, surface-acoustic wave filters [94], lasing devices [95] and as transparent conducting oxides [96]. ZnO is a compound semiconductor that has been researched since the mid-20<sup>th</sup> century, with reviews by various authors. Since the 1990s however, there has been an enormous resurgence in ZnO research leading to more recent reviews by Özgur *et al.* [97], Nickel and Terukov [98], Jagadish and Pearton [99] and Ellmer *et al.* [86, 100].

The two main properties of ZnO that interests optoelectronic researchers most are its wide direct bandgap of approximately 3.3 eV (at 300K) and high exciton binding energy of 60 meV. ZnO, with its wide tuneable bandgap has the potential to be used in light emitting diodes (LEDs) [101]. ZnO's large exciton binding energy is 2.4 times the thermal voltage  $\left(\frac{kT}{q}=26 \text{ meV}\right)$ , making it possible for efficient near band-edge excitonic emission at room or higher temperatures. Additional advantages of ZnO include: high energy radiation hardness, amenable to wet chemical etching and a wide variety of available deposition methods. The main drawback however, in terms of optoelectronic application, is the difficulty of producing high quality *p*-type ZnO, because in its intrinsic (undoped) form, ZnO is actually *n*-type. This is a prerequisite for many optoelectronic devices. The nature of the intrinsic *n*-type conductivity is presented later in this chapter.

#### 3.2.2 Basic Structural, Physical and Optical Properties of ZnO

Under normal ambient conditions, the thermodynamically stable phase of crystalline ZnO is the wurtzite structure. The ZnO wurtzite structure belongs to the hexagonal system which has two lattice parameters of a = 3.25 Å and c = 5.2 Å [102, 103] with a ratio  $\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633$ . It belongs to the space group  $C_{6v}^4$  or  $P6_3mc$ . A schematic representation of wurtzite ZnO is shown in Figure 3.2(a). The fourfold co-ordinated structure consists of two superimposed hexagonal close-packed (HCP) sub-lattices shifted along the c-axis. Each sub-lattice consists of four sample atoms per unit cell surrounded in a tetrahedral

fashion by four atoms of the other kind and vice versa. In addition, Figure 3.2(b) shows the different crystallographic orientations and surface planes (a-, r- and c-) for a crystal with a hexagonal structure.

Figure has been removed due to Copyright restrictions Refer to Fig. 3.1. in K. Ellmer, A. Klein, and B. Rech, "Transparent Conductive Zinc Oxide: Basics and Applications in Thin Film Solar Cells," in Springer Series in Materials Science 104, R. Hull, P. Jürgen, R. M. Osgood Jr., and H. Warlimont, Eds., ed: Springer Berlin Heidelberg, 2008, p. 82.

**Figure 3.2.** (a) Primitive cell and hexagonal prism of wurtzite structured ZnO lattice, where *a* and *c* are lattice constants. (b) Schematic drawing of a single crystal hexagonal prism showing the different surface planes (a-, r- and c-) and crystallographic orientations [104].

The basic properties of ZnO are given in Table 3.1 below. ZnO has a very high melting/boiling point under high pressure and only sublimes at atmospheric pressures above **1200** °C. The sublimation of ZnO happens correspondingly by decomposition to its gaseous constituent elements by the following equation.

$$ZnO(s) \rightleftharpoons Zn(g) + 0.5O_2(g) \tag{3.1}$$

For this thesis, this is the **most crucial** property of ZnO as it is annealed at temperatures up to 1100 °C together with SRO/SiO<sub>2</sub> superlattice films.

Properties	Unit	Value	Ref.
Chemical formula		ZnO	
Abundance in the earth's crust	ppm	40	[102, 103]
Crystal structure		Wurtzite	
Space group		$C_{6v}^4$ or $P_{6_3}mc$	
Lattice constant (at 300 K)	Å	a = 3.25	[102, 103]
		<i>c</i> = 5.2	
Co-ordination geometry		Tetrahedral	
Molar mass	g/mol	81.38	[105]
Density, $\rho$	g/cm <sup>3</sup>	5.67	[106]
Thermal conductivity, $\kappa$ (at 300 K)	W/m∙K	69∥, 60 <sup>⊥</sup>	[107]
Thermal expansion coefficient, $\alpha$ (at 300 K)	10 <sup>-6</sup> /K	2.92∥, 4.75⊥	[108]
Melting point	°C	1975 (decomposes)	[109]
Boiling point	°C	1975 (decomposes)	[109]
Sublimation point	°C	> 1200	[106]
Melting point of zinc	°C	420	[107]
Heat of formation, $\Delta H_f$	kJ/mol	-350.46 ± 0.27	[105]
Refractive Index, <i>n</i> (at 589 nm)		2.0034	[110]
Static dielectric constant, $\epsilon(0)$		8.75∥, 7.8⊥	[107]
Optical dielectric constant, $\epsilon(\infty)$		3.75∥, 3.70⊥	[107]

Table 3.1. Basic structural, physical and optical properties of zinc oxide

#### 3.2.3 Electrical Properties of ZnO

Intrinsic polycrystalline ZnO thin films, as mentioned above, have a large direct bandgap reported around 3.1 to 3.4 eV at room temperature. The electronic structure of tetrahedrally bonded compounds (e.g. ZnO) with wurtzite, diamond, zincblende or chalcopyrite arrangements are very similar [111, 112]. The wurtzite and zincblende configurations are almost identical apart from their symmetry. The cation and anion *s*- and *p*-orbitals create overlapping  $sp^3$ -hybrids which form bonding/anti-bonding combinations. Their valence band maximums are found from the anion *p*-states which are threefold degenerate, but the degeneracy is lifted by non-centrosymmetric crystal fields and spin-

orbit splitting. The valence band maximum can be derived using the linear combination of atomic orbitals, LCAO theory which uses the anion *p*-levels and their energy [111]:

$$E_V = \frac{\left(E_p^a + E_p^c\right)}{2} - \sqrt{\left\{\left[\frac{E_p^a + E_p^c}{2}\right]^2 + \left[\frac{1.28\hbar^2}{(m_e d^2)}\right]^2\right\}}$$
(3.2)

where  $E_p^a$  and  $E_p^c$  are the *p*-orbital energies of the anion and cation respectively,  $m_e$  is the free electron mass in the semiconductor and *d* is the inter-atomic spacing. Eq. (3.2) dictates that a larger valance band maximum is expected for anions with smaller *p*-level binding energies. The binding energies of the *p*-orbitals of oxygen, sulfur, selenium and tellurium (calcogens of group-16 in the periodic table) decreases monotonically from 16.72, 11.60, 10.68 and 9.54 eV respectively. This trend corresponds well with the band alignment diagram of II-VI semiconductors in Figure 3.3. However, complex interactions of the anion *p*-levels and cation *d*-levels shift the energy bands from their expected positions creating slight exceptions, e.g. ZnO (3.4 eV) has a slightly smaller bandgap than ZnS (3.7 eV).

Figure has been removed due to Copyright restrictions

Refer to Fig. 1.10. in K. Ellmer, A. Klein, and B. Rech, "Transparent Conductive Zinc Oxide: Basics and Applications in Thin Film Solar Cells," in Springer Series in Materials Science 104, R. Hull, P. Jürgen, R. M. Osgood Jr., and H. Warlimont, Eds., ed: Springer Berlin Heidelberg, 2008, p. 13.

**Figure 3.3.** Band alignment diagram for II-VI semiconductors derived using the density functional theory (DFT) calculations by Wei and Zunger [113]. The ZnS valence band maximum energy has been arbitrarily set to 0 eV [114].

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Even though ZnO has been under research for a few decades now, the true nature of the *n*-type conductivity in intrinsic (undoped<sup>‡</sup>) ZnO is still not fully understood. The general consensus attributes the residual background to intrinsic (or native) point defects. Intrinsic point defects cause deviations from the ideal crystalline structure through displacement or removal of lattice atoms, these are namely vacancies, interstitials and anti-sites. In terms of ZnO, these are denoted as  $V_{Zn}$  and  $V_O$ ,  $Zn_i$  and  $O_i$  and  $Zn_O$  and  $O_{Zn}$ , respectively. Some authors suggest that the Zn<sub>i</sub> is the dominant defect on the basis of ionic diffusion or size considerations as the Zn<sup>++</sup> ion has an ionic radius of only 74 pm whereas oxygen has an ionic radius of 138 pm [115-118]. Literature elsewhere suggest that the predominant defects are due to the V<sub>O</sub> through diffusion experiments [119], reaction rate calculations [120] and Hall effect measurements [121].

This means that the stoichiometry of the ZnO is very important in terms of its electrical properties. In most experimental cases, intrinsic ZnO samples seem to contain an excess of Zn, i.e. a deficiency in O [116]. That is in  $ZnO_{1-x}$ , *x* is typically between the ranges of 0 to 0.05. By varying the oxygen content of the crystals, for example by annealing at different oxygen partial pressures, the carrier concentration and hence conductivity will vary as shown by Wagner and Schottky [122] as well as Hauffe and Block [123]. The reaction balance equation between the zinc interstitials, Eq (3.3) or oxygen vacancies, Eq. (3.4) and the conduction band electrons are given below:

$$O_2(gas) + 2Zn^{"}(i) + 4e \Leftrightarrow 2Zn0 \tag{3.3}$$

$$O_2(gas) + 4Zn(l) + 20^{\circ}(v) + 4e \Leftrightarrow 2Zn0 \tag{3.4}$$

where *i*, *l* and *v* represent the interstitial position, lattice location and vacancy respectively. Furthermore, by applying the law of mass action the following equation is obtained:

$$[Zn^{"}(i)]^{2}[e]^{4}p_{O_{2}} = k \tag{3.5}$$

<sup>&</sup>lt;sup>‡</sup> To avoid confusion, the term "intrinsic" used in this thesis to describe ZnO refers to the fact that it is undoped.

where k is a constant. Now, given that only doubly charged zinc interstitials (or oxygen vacancies) provide donor electrons, a partial oxygen pressure dependence on the conductivity can be thus deduced as:

$$\sigma = [e] \cdot k' = p_{O_2}^{-\frac{1}{6}} \cdot k'$$
(3.6)

where *k*' is a constant. Experimentally, the exponent in Eq. (3.6) is not  $-\frac{1}{6}$ , but somewhere between  $-\frac{1}{4}$  and  $-\frac{1}{5.6}$  [123]. The lower than expected variation in conductivity is due to the porosity of the ZnO samples which were only 60-70% of the density of bulk crystalline ZnO.

Generally, the energy required to produce a point defect depends on the charge on the defect and the lattice site with which it wishes to occupy. In ZnO, vacancies or interstitials have a charge of  $\pm 2$  while anti-sites have a charge of  $\pm 4$ . Vacancies and interstitial dopants are more common and thus important in polar compounds like ZnO, whereas anti-site defects are more common in covalent compounds, for example in many III-V semiconductors [124-126]. In terms of energetics of native defects in a crystal, the formation energy for one mole of a defect,  $G_d$ , involves a change in total energy  $\Delta E_d$  (including chemical potential terms). The distribution of defects on available sites per unit volume,  $N_{sites}$ , raises the change in vibrational entropy  $\Delta S$  of the system. The free energy of formation in a crystal is given by [124]:

$$\Delta G_d = \Delta E_d - T \Delta S \tag{3.7}$$

At equilibrium and in the dilute limit, the concentration of defects is thus given by:

$$N_d = N_{sites} e^{\frac{-\Delta G_d}{k}}$$
(3.8)

In summary, the formation energies of the native defects have a strong effect on the chemical potential and Fermi level position in the bandgap [127]. The chemical potential is related to the concentration of the elemental species present. For example, for gases, an increase (decrease) in the partial pressure of oxygen will lower (increase) the  $\Delta G_d$  for defect reactions that add oxygen, O<sub>i</sub>, or remove zinc, V<sub>Zn</sub>, and vice versa. For defects that are charged, the Fermi level or chemical potential of electron (or holes) will shift due to its relation to the defect formation enthalpy.



**Figure 3.4.** Defect formation energy for common ZnO defects as a function of Fermi level calculated via the first-principles pseudopotential method by Kohan *et al.* [124]. The graph on the left (a), is for high and on the right (b), for low zinc partial pressure. The 0-axis of the Fermi level is fixed at the top of the valence band.

Improvements in computational modelling methods in recent times have led to firstprinciple studies to derive the formation enthalpies of ZnO intrinsic point defects [124-126, 128-130] and to elucidate the exact nature of the intrinsic *n*-type doping nature in ZnO. Figure 3.4 shows results from such a study by Kohan *et al.* [124]. The horizontal lines correspond to neutral defects and the positive and negative slopes correspond to charged donors or acceptors, respectively. The kinks in the curves correspond to a change in the charge state for a particular species. From Figure 3.4, the donor that has the lowest formation enthalpy is the oxygen vacancy, V<sub>o</sub> and the acceptor with the lowest formation enthalpy is the zinc vacancy, V<sub>zn</sub>. This particular case is typical of "Frenkel" defect behaviour. Note, for Figure 3.4, there are two types of interstitial defect sites for the wurtzite ZnO structure: one is octahedrally co-ordinated denoted as (oct) and the other by default is tetrahedrally co-ordinated. In addition, negative defect formation enthalpies means that the system is unstable and spontaneous defect formation will occur. Typically, the Fermi energy shifts up (down) with donor (acceptor) doping, thus decreasing the formation enthalpy of intrinsic acceptors (donors). This is a well-known self-compensation mechanism in many semiconductors which limits the Fermi level movement and a limitation to the doping. An important issue that is often encountered is the loss in electron concentration when donor doped ZnO becomes compensated by high oxygen content which leads to the increase in  $V_{zn}$ .

Overall, despite all the computational modelling analysis and practical experimental research there is still **no consensus** for the intrinsic *n*-type conductivity in ZnO. It is understood, that the V<sub>0</sub> is a deep donor and cannot deliver enough carriers due to its large ionization energy, but on the other hand the Zn<sub>i</sub> has low ionization energy, but a relatively high formation enthalpy, hence their concentration is relatively lower. A possible factor that may have been overlooked is the significance of the role of hydrogen which is known to play a role as shallow donors in intrinsic ZnO. Hydrogen is always present in all growth methods of ZnO due to its small size and high diffusivity. Hydrogen in ZnO has been investigated via first-principle calculations [124, 131, 132]. The unique attribute of hydrogen in ZnO, is that it occurs exclusively as a donor, whereas in other semiconductor materials, hydrogen can be amphoteric, which means that it occurs as H<sup>+</sup> in *p*-type and H<sup>-</sup> in *n*-type materials. The defect formation energy of hydrogen is relatively low at only 1.56 eV and ionization energy of approximately 30 meV [124, 131-134].

To conclude this section, Table 3.2 on the next page lists the basic electrical properties of ZnO:

Properties	Unit	Value	Ref.
Bandgap (at 300 K)	eV	3.1 - 3.4 (direct)	[76, 86, 135-
			137]
Binding energy	meV	60	[97, 138]
Static dielectric constant, $\frac{e_s}{e_0}$		8.4 - 8.5	[76, 139]
Effective electron mass in conduction		0.27 <i>⋅m</i> ₀	[76]
band, $m_e^{\cdot}$			
Effective hole mass in valence band, $\dot{m_h}$		1.8∙ <i>m</i> ₀	[139]
Electron affinity	eV	4.35	[137]
Work function	eV	4.35 - 4.45	[137, 140,
			141]
Donor level, $E_C - E_D$	eV	0.03	[142]
Effective conduction band density of	/cm <sup>3</sup>	3.7 × 10 <sup>18</sup>	[86]
states, $N_c$ (at 300 K)			
Electron mobility (at 300 K)	cm²/V⋅s	120 - 440	[97]
Hole mobility (at 300 K)	cm²/V·s	180	[76]

#### Table 3.2. Basic electrical properties of zinc oxide

Note, some parameters such as bandgap, mobility, carrier density and conductivity have large variances, simply because as explained in the previous sections, these values depend on issues such as: whether the ZnO is bulk single crystal, polycrystalline or thin film; how they were prepared and of course their stoichiometry.

#### 3.2.4 Extrinsic Doping of ZnO

Extrinsic doping of ZnO almost always occurs as *n*-type. *N*-type doping of ZnO is simple; however there is still difficulty in achieving *p*-type doping. *N*-type conductivity of ZnO can be controlled by intrinsic doping, i.e. creation of intrinsic donors through point defects or through extrinsic doping. As explained in the last section, intrinsic doping can be realised through adjusting the stoichiometry of the ZnO during the deposition or post-annealing in vacuum or a hydrogen-containing (reducing) atmosphere. However, there is a limit to the conductivity of intrinsically defect doped films, which is only about  $10^{-2}$  to  $10^{-3} \Omega cm$  [100] and the electrical properties of the films are often unstable due to the re-oxidation of the

sub-stoichiometric  $ZnO_{1-x}$ , where *x* is between 0-0.05 [143]. Therefore, for more controllable and stable *n*-type conductivity, extrinsic doping is used. Extrinsic doping can be achieved either through the substitution of anions on oxygen lattice sites and/or cations on zinc lattice sites. The latter doping method is much more common. Much higher carrier concentrations and thus higher *n*-type conductivities can be achieved through extrinsic doping. The most common dopants for ZnO are the group-III trivalent elements: Al, B, Ga and In [100]. Aluminium is the most common dopant for ZnO due to its high incorporation levels and low resistivity.

Dopants are commonly incorporated into the films in the form of oxides, such as the group-III oxides:  $AI_2O_3$ ,  $B_2O_3$ ,  $In_2O_3$  and  $Ga_2O_3$ . It is assumed that the dopants substitute the zinc lattice sites providing the conduction band with one additional electron not required in the bonding, shown by the following equation:

$$M_2 O_3 \Leftrightarrow 2M_{Zn} + 2e + 2O_0 + \frac{1}{2}O_2 \tag{3.9}$$

where M represents a group-III metal. Other oxides with three or even four valence electrons can be used to increase the conductivity of ZnO. The oxygen partial pressure dependence equality is shown below:

$$[e] = [M_{Zn}] \sim p_{O_2}^{-\frac{1}{8}}$$
(3.10)

This equality shows that extrinsically doped ZnO at high oxygen partial pressures or annealing in high oxygen environments unfortunately results in high resistivity. A plausible explanation is the formation of zinc vacancies due to their low enthalpy of formation in oxygen-rich conditions (see Section 3.2.3).

#### 3.2.5 Carrier Transport Properties in Polycrystalline ZnO Thin films

Ionised impurity scattering, which is the most important scattering mechanism in doped ZnO, describes the scattering of free carriers via the screened Coulomb potential of fix charged impurities or defects. It is well known that an increase in extrinsic doping results in an increase in fixed charges which increases the scattering of free carriers and thus decreases the mobility. For further information on the types of scattering mechanisms please refer to Chapter 2 of Ref. [144] and references therein. Another factor that affects the mobility is grain boundaries or barriers which are inherent in polycrystalline films. The amount of grain barriers depends on the size and shape of the film's grains. Grain barriers result in crystallographically disturbed regions which lead to electronic defects in the semiconductor's bandgap.

Figure has been removed due to Copyright restrictions

Refer to Fig. 2.14. in K. Ellmer, A. Klein, and B. Rech, "Transparent Conductive Zinc Oxide: Basics and Applications in Thin Film Solar Cells," in Springer Series in Materials Science 104, R. Hull, P. Jürgen, R. M. Osgood Jr., and H. Warlimont, Eds., ed: Springer Berlin Heidelberg, 2008, pp. 62.

**Figure 3.5.** (a) mobilities and (b) resistivities of various doped and intrinsic ZnO thin films vs. the carrier concentration compiled by Ellmer in Refs. [143, 144] and references therein. The thin films were deposited by various methods including: magnetron sputtering (all squares), MOCVD (open diamond) and PLD (open circle). The different lines represent different theoretical estimations.

Figure 3.5 shows a compilation by Ellmer [143, 144] of various mobility and resistivity values versus carrier concentration for doped and intrinsic ZnO thin films prepared by magnetron sputtering, metalorganic chemical vapour deposition (MOCVD) and pulsed laser deposition (PLD) in the last 25 years. From Figure 3.5(b) the lowest doped ZnO resistivities are in the range of  $1.5 \times 10^{-4}$  to  $3 \times 10^{-4}$   $\Omega$ cm, which is still a little higher than the lowest reported ITO resistivity of  $1.2 \times 10^{-4}$   $\Omega$ cm [145]. The maximum mobility is

around 50-60 cm<sup>2</sup>/Vs. Although doped ZnO has been researched extensively for over three decades, with improvements such as larger grain sizes and higher dopant incorporation rates, there have not been significant breakthroughs in increasing the mobility or reducing the resistivity. This issue points universally to ionised-impurity scattering, which puts a constraint on the mobility of degenerately doped ZnO as well as other TCOs. The highest reported carrier concentration in doped ZnO thin films is 1.5 ×  $10^{20}$  /cm<sup>3</sup> and this is already close to the solubility limit of group-III dopants in ZnO [146]. In most cases there is in fact an optimum dopant concentration that yields the lowest resistivities. Using high doping to lower the resistivity may seem intuitive; however another problem is introduced with higher carrier concentrations, which is the free carrier absorption in the long wavelengths [147]. Therefore there is a trade-off between increasing the dopant concentration, the mobility, resistivity and the transmittance of the TCO.

#### 3.2.6 Types of Deposition Methods

ZnO thin films can be prepared by various deposition methods including:

- Non-reactive magnetron sputtering [references provided in Table 7.1 of Chapter 7]
- Reactive magnetron sputtering [148-155]
- Sol-gel spin or dip coating [156-168]
- Metalorganic chemical vapour deposition [90, 169]
- Pulsed laser deposition [170, 171]
- Electron beam evaporation [172, 173]
- Spray pyrolysis [158, 174]
- Thermal plasma [175]

The method that is used to fabricate ZnO and AZO thin films in this thesis is **non-reactive radio frequency (RF) magnetron sputtering**. A literature review survey of RF magnetron sputtered-deposited AZO thin films is given in Section 7.2 of Chapter 7.

### 3.3 Summary

Transparent conducting AZO is a useful material in thin-film photovoltaics. It allows light to pass through to the active material underneath as well as transport photogenerated current out of the photovoltaic device. In addition AZO can act as anti-reflection coatings or be textured to provide light scattering [152, 176-178]. The basic structural, electrical and optical properties of ZnO were discussed in Section 3.2. The **most crucial** property of ZnO in terms of the work in this thesis is that it does not decompose when annealed at 1100 °C. The *n*-type intrinsic nature of ZnO was explained as well as the difficulty in achieving *p*-type ZnO. Degenerate extrinsic doping of ZnO leads to very low resistivity films, however there is a fundamental physical limit to this resistivity due to the effect of ionized impurity scattering which is the most important scattering mechanism.

# Chapter Four: Fabrication and Characterisation Techniques

### 4.1 Introduction

This chapter gives an overview of the different fabrication, materials characterisation and photovoltaic device characterisation techniques used in this thesis. The overviews start with a general introduction to each of the techniques followed by their purpose and relevance to the research in this thesis. The materials characterisation section (Section 4.3) is arranged beginning with the structural characterisation followed by the optical and then the electrical characterisation techniques. Please refer to the contents page at the start of this thesis for the comprehensive list of fabrication and characterisation techniques used in this work. The key techniques used in this thesis such as radio frequency (RF) magnetron sputtering, high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), have slightly more detailed explanations.

### 4.2 Fabrication Techniques

#### 4.2.1 RF Magnetron Sputtering

In this thesis, the key deposition tool is RF magnetron sputtering. Sputtering is a technique where thin film materials are deposited onto a surface (i.e. substrate). The sputtering process involves the formation of gaseous plasma from an inert gas such as argon (Ar) and the ions in the plasma are then accelerated onto a 'target'. The target is eroded by the high energy ions and neutral particles are continuously ejected from the target in the form of either atoms, a collection of atoms or molecules. These neutral particles travel in a straight line towards the substrate surface to produce a thin film comprised of the target material [179]. RF generators with a frequency of 13.56 MHz are connected to the cathode targets via an impedance matching network consisting of variable capacitors. "Magnetron" sputtering is an improved process to sputtering where a magnet is utilised behind the target to create a magnetic field directly above the target surface which traps free electrons that cause unwanted bombardment of the substrate surface as well as improve

the efficiency of the gaseous plasma formation (i.e. ionising the neutral gas) and hence of the sputtering process. Figure 4.1 shows a schematic diagram of a typical RF magnetron sputtering system.



Figure 4.1. Schematic diagram of a typical RF magnetron sputtering system.

The instrument used in this work is a computer-controlled AJA ATC-2200 magnetron sputtering system. In this thesis, thin films of silicon rich oxide (SRO), silicon dioxide (SiO<sub>2</sub>), zinc oxide (ZnO) and aluminium doped zinc oxide (AZO) are all deposited in this manner. RF magnetron sputtering is the preferred technique due to the easily controllable and stable deposition rates, ability to co-sputter multiple targets and ability to produce thin films with good compositional and structural uniformity. The types of solid targets used in this thesis are Si, SiO<sub>2</sub>, B, P<sub>2</sub>O<sub>5</sub>, ZnO and ZnO:Al (ZnO + 2% wt. Al<sub>2</sub>O<sub>3</sub>). The three main control parameters during the sputtering process are: 1) the Ar working pressure, 2) the power of the RF sources and 3) the sputtering time. The substrate heating temperature is

used for the deposition of ZnO and AZO. An increase in RF power will increase the deposition rate. The thickness of the deposited layers is given by the following equation:

$$d_{thin\,film} = R_{dep} \times t_{dep} \tag{4.1}$$

where,  $R_{dep}$  is the deposition rate and  $t_{dep}$  is the deposition time. For the work in this thesis, the thickness of the thin films and the deposition rates are calibrated externally via spectroscopic ellipsometry (SE) measurements and modelling. External calibration via SE is more accurate than the in-built crystal monitor and it allows the calibration of co-sputtering rates. SRO is created by co-sputtering Si and SiO<sub>2</sub> targets and if doping is required, B or P<sub>2</sub>O<sub>5</sub> targets are also co-sputtered.

#### 4.2.2 Furnace Annealing

The formation of Si nanocrystals (NCs) in this thesis requires high temperature annealing ( $\approx$ 1100 °C) of the deposited superlattice thin films [53]. The equation for the phase separation of Si and SiO<sub>2</sub>, nucleation and subsequent formation of the Si NCs can be found in Section 2.4 of Chapter 2. AZO thin films are also annealed at high temperatures in this thesis. An inert gas such as nitrogen (N<sub>2</sub>) or Ar is used to avoid extensive oxidation. Forming gas (96% Ar or N<sub>2</sub> + 4% H<sub>2</sub>) is also employed to assist in the annealing process.

The primary annealing apparatus is a conventional quartz tube furnace. The furnace used in this thesis is an MTI OTF-1200X quartz tube furnace with programmable functions. The properties of the samples can be affected by the following: 1) the temperature of the annealing, 2) the annealing time and 3) the cleanliness of the quartz tube, boat and/or sample. Two tubes are used: 1) a dedicated tube for annealing the SRO/SiO<sub>2</sub> superlattice thin film samples and 2) a general annealing tube for annealing AZO thin films and other samples (e.g. ones that include metals).

#### 4.2.3 Metallisation

The metallisation for this thesis was done by the common physical vapour deposition (PVD) method of thermal evaporation. Thermal evaporation of metals is a simple process

where a metal is heated above its boiling point/vapour pressure in an evacuated chamber [79]. The evaporated metal then travels at high velocity in a straight-line trajectory to condense onto a substrate some distance away. The metal is heated by means of a resistive heater, electron gun or pulsed laser heating. The evaporation takes place in a vacuum chamber so the evaporated particles have a long mean free path to travel to the deposited substrate without colliding with the background gas molecules. Patterned masks can be made for specific metal contact designs. The thermal evaporator used in this thesis is an INTERCOVAMEX H2 PVD/PECVD system, which is used for making Al contacts for the solar cell devices in Chapter 9.

### **4.3 Materials Characterisation Tools**

#### 4.3.1 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a well-known technique where electrons are transmitted through an ultra-thin specimen (typically below 100 nm). The accelerated electrons interact with the specimen as they pass through allowing an image to be formed and magnified onto an imaging device such as a charge-coupled device (CCD) camera or fluorescent screen. Most TEMs nowadays operate at high voltages between 100–400 kV [180]. TEM has significantly higher resolution than light microscopy owing to the shorter de Broglie wavelength of the electrons. It is a very powerful imaging tool that allows the study of the sample microstructure, crystallography of phases, lattice defects, microchemical material properties and can allow the acquisition of atomic resolution images. TEM is one of the most common analysis techniques in many scientific fields and can come in several different forms denoted by different acronyms such as HRTEM (high resolution transmission electron microscope), S/TEM (scanning transmission electron microscope) and EFTEM (energy-filtered transmission electron microscopy) [180].

Three forms of filaments create the electrons which accelerate through the TEM column: 1) tungsten, 2) lanthanum hexaboride  $(LaB_6)$  and 3) field emission. The first two are thermionic emitters and the field emission is based on electron tunnelling. Usually a TEM equipped with a field emission gun (FEG) emits the finest and most intense beam of the three forms and thus allows the highest spatial resolution and reduces problems such as aberration. There are three types of FEGs: cold, thermal or Schottky with different advantages and disadvantages. The work in this thesis requires HRTEM as detail down to the nanometre scale is studied, hence the instruments used in both Chapter 5 and Chapter 6 are FEG based HRTEMs. The resolution of HRTEM is limited by: 1) the brightness of the electron beam, 2) chromatic aberration and most importantly 3) spherical aberration due to the electron source geometry as a manifestation of inconsistencies in the objective lens system. Fortunately, the spherical aberration can be reduced by installing multipole correctors in the microscopes. The limit of resolution of a particular HRTEM can be compared in several ways. A common method is to use the contrast transfer function cutoff [181]:

$$q_{max} = \frac{1}{0.67 \cdot (C_S \lambda^4)^{\frac{1}{4}}}$$
(4.2)

where,  $C_{\rm S}$  is the spherical aberration correction,  $\lambda$  is the wavelength of the electrons. So for example, a 200 kV aberration corrected HRTEM with a  $C_{\rm S}$  of 1 µm would have a best theoretical cut-off of 42 pm whereas the same HRTEM without aberration correction would only have a theoretical cut-off of around 200 pm (with a  $C_{\rm S}$  of 0.5 mm).

As mentioned above, a TEM specimen should be fairly thin (<100 nm) to allow sufficient electron transmission and improved resolution. Specimen preparation is therefore an important step in good HRTEM. Specimen preparation is often tricky and requires a significant amount of time relative to the actual HRTEM imaging. Typical methods include manual mechanical thinning and ion milling/slicing by focused ion beam (FIB). FIBs which allow local sputtering and generation of thin sections use Ga ions rather than electrons as their medium. Another method for samples deposited on Si wafers is the small angle cleavage technique [182].

Chapter 5 uses *in situ* HRTEM microscopy with real-time specimen heating. The special instrument that can conduct this type of experiment is the aberration-corrected FEI Titan 800-300 keV FEG S/TEM system. There are only a few of these systems around the world, one of which was used in this thesis and is housed at MIKA, the Electron Microscopy Centre of Materials Science and Engineering Faculty at the Technion – Israel Institute of Technology. This type of real-time HRTEM imaging is used to study the growth

and nucleation kinetics of Si NCs via *in situ* annealing using a heating stage accessory inside the specimen chamber of the microscope.

Chapter 6 uses HRTEM and EFTEM. The advantage of EFTEM is that it has the ability to provide higher spatial resolution information on the chemistry and composition of the specimen being imaged [183]. This is especially useful when studying the structural properties of NCs, thin films and interfaces. The second microscope used for this purpose in this thesis is the JEOL 200 kV FEG 2200FS.

#### 4.3.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is another type of electron microscope where the electron beam from a thermionic, Schottky or field-emission cathode is scanned across the specimen. The potential difference between the cathode and anode can be from as low as 0.1 keV to as high as 50 keV [184]. Although SEM does not have the same resolution limits as HRTEM, SEM is a simpler and quicker tool for observing the topography and surface morphology of samples down to a few nanometres [185]. The electron beam is usually scanned in a raster pattern where the beam's position is combined with the detected signal (usually secondary electrons, backscattered electrons and x-rays) to produce an image. In addition, elemental and compositional information can be obtained by SEM using in-built techniques such as energy dispersive x-ray spectroscopy (EDS). A FEI Nova nanoSEM 230 field-emission scanning electron microscope (FE-SEM) is used in Chapter 7 to observe the surface morphology of annealed AZO thin film and together with XRD to estimate its grain size.

#### 4.3.3 Atom Force Microscopy

Atom force microscopy (AFM), which is sometimes termed scanning force microscopy, is a type of microscopy that uses a tiny physical probe or sharp tip to scan the surface of a sample [186]. The advantage of AFM is that it has a very high resolution limit in the order of fractions of a nanometer which is more than 1000 times greater than that of the optical diffraction limit. It is a non-destructive technique that works by measuring the attractive and repulsive forces with the probe and the sample whilst scanning across the sample surface to produce real space 2D and 3D images. There are three main AFM operating modes: 1) contact, 2) non-contact and 3) tapping mode. The AFM instrument used in Chapter 7 is the
Bruker Dimension ICON SPM and its main purpose is to measure the surface roughness of AZO thin films before and after annealing at different temperatures and after various treatments.

### 4.3.4 X-ray Diffraction

XRD is a fast and simple non-destructive characterisation technique for analysing the crystalline phases of thin films and structural information such as the preferred orientation and average grain size [187]. X-ray diffractometry is based on the Bragg equation [188]:

$$n\lambda = 2d\sin\theta \tag{4.3}$$

where, *n* is an integer,  $\lambda$  is the wavelength of the X-ray, *d* is the spacing between the diffracted planes and  $\theta$  is the angle of incidence. XRD works by varying the incidence angle,  $\theta$  (i.e. the angle between the X-rays and the surface of the sample) over a specific range and measuring the reflected intensity as a function of  $2\theta$ . This type of scan, which is the most common scan used in XRD, is called the  $\theta$ - $2\theta$  scan. Particular diffraction peaks are observed, at particular *d*-spacing values (particular  $2\theta$  Bragg angles) where constructive interference from specularly reflected X-rays occur. Polycrystalline thin films consist of many grains with different orientations so diffraction occurs from those grains that happen to have an orientation which satisfies the Bragg condition.

The average crystallite or grain size of a thin film material can be estimated via the Scherrer equation [189]:

$$L = \frac{K\lambda}{\beta\cos\theta} \tag{4.4}$$

where, *K* is a dimensionless shape factor which has a typical value of 0.9, but varies with the type of crystallite,  $\lambda$  is the wavelength of the X-rays,  $\beta$  is the line broadening at half

maximum or full width at half maximum (FWHM) in radians and  $\theta$  is the centre of the peak in degrees (i.e. Bragg angle).

Measurements of thin films (1-1000 nm) using the conventional  $\theta$ -2 $\theta$  scan generally produce a weak desired signal from the actual thin film and a strong unwanted signal from the substrate [190]. Grazing incidence XRD (GIXRD) is a special technique that avoids this problem by using a fixed angle of incidence which is chosen to be slightly above the critical angle for total reflection of the thin film material and only the detector moves during the measurement scan. The XRD instrument used throughout this thesis is the PANalytical Xpert Materials Research Diffractometer (MRD). GIXRD is used to study the SRO/SiO<sub>2</sub> bilayer superlattice thin films and to estimate the average size of the Si NCs in Chapter 6 and in Chapter 7 it is used to study the preferred crystal orientation and average size of the AZO grains before and after annealing.

## 4.3.5 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) or ESCA (electron spectroscopy for chemical analysis) is a surface chemical analysis technique [191]. XPS is a widely used due to its comparative ease and data interpretation. It can measure the elemental composition in the vicinity of parts per thousand ( $\approx$ 0.1%) as well as analyse the empirical formula, chemical and electronic state of the elements within a material. The XPS method works by irradiating a sample surface with known monoenergetic X-rays, with photon energy, *hv*, which cause the emission or ejection of electrons. The ejected electrons must have sufficient energy to overcome the elements in the sample is made by measuring the kinetic energy (KE) of these ejected electrons which is given by the following equation:

Kinetic Energy (KE) = Photon Energy (
$$hv$$
) – (Binding Energy (BE) +  $\phi$ ) (4.5)

Or more commonly rearranged and presented as:

$$E_{binding} = E_{photon} - (E_{kinetic} + \Phi)$$
(4.6)

where,  $E_{binding}$  is the binding energy of the electron,  $E_{photon}$  is the energy of the X-ray photons,  $E_{kinetic}$  is the kinetic energy of the ejected electron and  $\Phi$  is the work function which is dependent on the spectrometer and element. The binding energy depends on both the element and the orbital shell from which the electron is ejected. XPS allows a binding energy spectrum with various peaks to be generated. In addition, information on the chemical or molecular species can be obtained by analysing subtle changes in binding energy. A quantitative analysis can be performed through the integration of the peak intensities, however this is quite complex and includes many corrections and requires careful expert interpretation. Depth profiling and/or surface sputter cleaning is usually possible by thinning using Ar ion guns in an XPS instrument. Finally, it should be pointed out that XPS has poor lateral resolution but good depth resolution and only elements from Li upwards can be analysed. The XPS instrument used in this thesis is a Thermo ESCALAB250Xi X-ray photoelectron spectrometer. Its purpose is to measure the elemental composition of the AZO films in Chapter 7 before and after annealing at various temperatures in N<sub>2</sub> up to 1100 °C.

#### 4.3.6 Time-of-Flight Secondary Ion Mass Spectrometry

Secondary ion mass spectrometry (SIMS) is based on the analysis of charged particles (i.e. secondary ions) ejected from a sample surface when sputtered by a primary beam of ions. The interaction of the primary sputtering beam with the sample surface causes three effects: 1) mixing of the upper layers of the sample resulting in amorphisation; (2) implantation of the sputtered ions and (3) ejection of secondary ions which include atoms, ions and molecules from the surface of the sample being analysed. The ejected species can be electrically neutral or charged species (ions), but only charged ions can be detected. The emission of different species depends on their ionisation potential which can vary by several orders of magnitude depending on the bonding state of the species. The mass/charge ratios of these secondary ions are collected and measured with a mass spectrometer to determine the elemental, isotopic, or molecular composition of the surface at a depth of typically 1 to 2 nm although resolution down to 1-3 monolayers is possible.

Normally SIMS is regarded as a qualitative technique, however quantitative measurements are possible by calibration with the standards with known elemental composition. SIMS is an extremely sensitive surface analysis technique, with elemental detection limits ranging from the ppm to ppb level (i.e.  $10^{12}-10^{16}$  atoms/cm<sup>3</sup>) [192]. Another major advantage of SIMS is that all elements in the periodic table, even down to H, can be detected.

A typical SIMS instrument consists of: 1) an ultra-high vacuum system, 2) a primary beam source (typically O<sup>-</sup>, O<sub>2</sub><sup>+</sup>, Cs<sup>+</sup>, Ar<sup>+</sup> or SF<sub>5</sub><sup>+</sup>) (the type of beam source depends on the required current, beam dimensions and most importantly on the sample being analysed), 3) a flood gun for analysis of insulators, 4) a method of collecting the ejected secondary ions, 5) a mass analyser to isolate ions of interest and 7) an ion detection system to record the magnitude of the secondary ion signal (typically a CCD camera and image plate).

Time-of-Flight secondary ion mass spectrometry (ToF-SIMS) is a special type of SIMS where the mass spectrum is detected and acquired in parallel rather than series. The unique time-of-flight mass analyser is able to accelerate the sputtered secondary ions into a "flight tube" and their mass is determined by measuring the exact time at which they reach the detector (i.e. time-of-flight). ToF-SIMS is quicker than SIMS and has a high signal to noise ratio and thus has better sensitivity. It is often the best method of choice for elemental depth profiling analysis of thin films. The instrument used in this thesis is the IONTOF GmbH TOF.SIMS5 which is equipped with equipped with a reflectron TOF analyser giving high secondary ion transmission with high mass resolution, a sample chamber with a 5-axis manipulator (x, y, z, rotation and tilt) for flexible navigation, a fast entry load-lock, charge compensation for the analysis of insulators, a secondary electron detector for SEM imaging, a state-of-the-art vacuum system and an extensive computer package for automation and data handling [193]. ToF-SIMS is used in Chapter 8 to obtain an elemental depth profile of the AZO superstrate Si QD solar cell device.

### 4.3.7 Raman Spectroscopy

Raman spectroscopy is a fast and non-destructive technique based on the inelastic scattering of monochromatic light by matter [194], typically from a laser source (most commonly in the IR, visible or UV range). When a photon of light that is too small to excite an electronic transition in a particular molecule (instead it interacts with optical phonon(s)),

it can be scattered in one of three ways: 1) elastic scattering retaining its incident energy, or inelastic scattering (i.e. the frequency of the incident photon changes) by either 2) giving up or 3) removing energy from the molecule [194]. The frequency of the re-emitted photons is shifted up or down in relation to the incident photon frequency and this is termed the Raman effect. This shift provides specific information regarding the vibrational, rotational and other low frequency transitions in molecules of the sample. Multi-channel detectors such as a photodiode array (PDA) or a CCD are used to detect the re-emitted Raman scattered light. A spectrum presented as a wavenumber shift (cm<sup>-1</sup>) versus the intensity is obtained. The Raman instrument used for this thesis is the inVia (Renshaw) confocal microscope system. A green 514.4 nm wavelength  $Ar^+$  laser is used as the excitation source. Raman spectroscopy is used in Chapter 6 for estimating the crystalline to amorphous Si ratio in the SRO/SiO<sub>2</sub> bilayer superlattice thin films.

#### 4.3.8 Spectrophotometry (Reflection, Transmission and Absorption)

Optical measurements are one of the most common and important measurements when it comes to investigating the properties of thin films in photovoltaics. A spectrophotometer is used to quantitatively measure the transmission and reflection of a thin film. Photometers measure the light beam's intensity as a function of wavelength which is created by lamp(s) and a monochromator. The important features of a spectrophotometer are its spectral bandwidth (the range of wavelengths it can transmit through a sample) and the measured percentage transmission/reflection of the sample. The optical absorption at a particular wavelength of a thin film is given by the following equation:

$$A = 1 - (T + R) \tag{4.7}$$

where T and R denote the fraction of light that is transmitted and reflected at a particular wavelength respectively. Additionally, other properties of the thin films can be inferred from spectrophotometry measurements such as optical bandgap, film thickness, internal quantum efficiency (IQE), free carrier concentration in the film, etc.

The thin films in this thesis were measured with a UV/Vis PerkinElmer Lambda 1050 spectrophotometer system equipped with two light sources: 1) a deuterium lamp which generates light in the ultraviolet (UV) and 2) a tungsten lamp that generates light in the visible and near infrared (Vis/NIR) spectral range. The system also contains a doublebeam double-monochromator with a set of focusing mirrors and lenses to split the light into specific wavelengths. The double-beam spectrophotometers have the advantage that fluctuations in the lamp intensity do not affect the measurement as a reference signal can be taken continuously throughout the scan. Three different accessories/modules are available for this instrument, albeit only the integrating sphere accessory is used. An integrating sphere is an optical component comprising of a hollow spherical cavity with a diffuse white reflective coating for the interior walls and small openings for entry and exit of light beams. An integrating sphere allows the measurement of the absolute transmission, reflection and absorption of diffusely scattering thin film samples. The PerkinElmer integrating sphere accessory consists of a 150 mm diameter InGaAs sphere with a photomultiplier tube PMT detector for the UV/Vis range (up to 900) and a thermoelectrically cooled InGaAs Photodetector for the NIR range (860-2500 nm). The white highly reflective and diffuse material on the inside walls of the integrating sphere are made of Spectralon<sup>®</sup>.

#### 4.3.9 Spectroscopic Ellipsometry

Spectroscopic ellipsometry (SE) is an extremely sensitive characterisation technique which uses polarized light to characterise thin films, surfaces and material microstructure [195]. SE is most commonly used to determine thin film thicknesses and optical constants, although it is certainly not limited to these purposes. The sensitivity of SE can be down to the sub-monolayer range. However, the biggest disadvantage with SE is that it is an indirect measurement technique and the acquired experimental data must be fitted to a model, with the fit parameters providing the desired information [195]. In other words, SE is extremely precise, but its accuracy depends on the users' interpretation and modelling of the properties at hand. The Levenberg-Marquardt multivariate regression algorithm is typically used for model fitting process. The more that is known about the physical parameters before the model fitting, the better because the model fit should more accurately represent the true physical nature of the sample. Sometimes in order to verify the SE model another characterisation technique, which usually takes more time and

resources, is required. SE works by measuring the polarization state of a beam of light after it travels through an optical system, i.e. a thin film. The measured values are expressed as Psi ( $\Psi$ ) and delta ( $\Delta$ ) in the following equation [195]:

$$\rho = \frac{R_p}{R_s} = \tan(\psi) e^{i\Delta}$$
(4.8)

where,  $R_p$  and  $R_s$  are the Fresnel reflection coefficients for *p*- and *s*- polarised light respectively. Because SE works by measuring the ratio between the two values  $R_p$  and  $R_s$ , SE can be extremely accurate and repeatable.

The variable angle spectroscopic ellipsometer (VASE) used in this thesis is the M-2000VI VASE from J.A. Woollam Co. Inc. VASE and modelling is used in this thesis to measure the deposition rates of all the magnetron sputtered thin films as well as study the structural properties of the AZO thin films.

#### 4.3.10 Photoluminescence

In photovoltaics research, photoluminescence (PL) is a widely used technique which involves the radiative emission of photons from a semiconductor when it is illuminated by a light source (usually a monochromatic laser with higher photon energy than the bandgap of the semiconductor). The radiative process or in other terms, the inverse absorption of photons [196] happens when an electron occupying a higher energy level makes a transition down to an empty lower-energy state. A 'radiative' emission is when a photon with energy equal to the difference between the energy states is emitted, whereas a 'non-radiative' transition involves the emission in the form of heat via phonons. PL is commonly used to study the electronic bandgap of Si NC materials although the exact mechanisms of PL from Si NCs are still subject to debate [62, 197]. The photon energy at the centre of the broad Si NC peak in the PL spectrum is often conveniently taken as an estimation of the material's bandgap. PL of Si NCs is used to study Si NCs in Chapter 6 using an in-house built system with a 405 nm violet-blue laser as the excitation source. The PL signal detection is captured by a Si CCD camera. The PL measurements are usually corrected

by normalisation for the spectral response of the system and the PL spectrum is usually given in emission intensity versus wavelength or intensity versus photon energy.

## 4.3.11 Four-Point Probe and Hall Measurements

Fast electrical characterisation of semiconductor materials can be done by four-point probe (4-PP) and Hall Effect measurements. 4-PP measurements work by passing current through two outer probes and voltage through two inner probes which allow the measurement of substrate resistivity [198] as shown in Figure 4.2.



Figure 4.2. 4-PP sheet resistivity measurement of the *n-p* solar cell [198].

The sheet resistivity is calculated from the follow equation [199]:

$$\rho_{\Box} = \frac{\pi}{\ln 2} \cdot \frac{V}{I} \tag{4.9}$$

To measure the bulk resistivity, the sheet resistance value is multiplied by the thickness, t of the thin film layer or wafer:

$$\rho_{\Box} = \frac{\pi}{\ln 2} \cdot \frac{V}{I} \cdot t \tag{4.10}$$

where, *t* is the thin film layer or wafer thickness in cm.

Measurement problems are often encountered when taking 4-PP measurements. A Schottky diode (rather than an ohmic contact) may be formed between the metal probes and the semiconductor. Very high or very low resistivity samples require adjustment of the current between the two outer probes to obtain reliable readings [198]. The 4-PP instrument used in this thesis is the Jandel RM3 system. The upper voltage limit is set at 150 mV and the minimum current is set at 10 nA. The most accurate readings can be obtained when the current is set at a point where the voltage reading is closest, but not surpassing 150 mV.

The Hall measurement technique allows the determination of the electrical resistivity, carrier density and mobility as well as the carrier type in semiconductor materials [200]. It is based on the Hall Effect discovered by Edwin H. Hall in 1879 [201]. The Hall Effect occurs when a current carrying conductor placed in a perpendicular magnetic field generates a voltage in the conductor that is perpendicular to both the magnetic field and the current. The most common Hall measurement technique involves the van der Pauw technique [202, 203] which works by contacting a thin-plate sample (around 1 cm × 1 cm) on four small ohmic contacts placed on the four corners of the sample. Firstly a series of resistivity measurements are taken to measure the sheet resistivity using the method outlined for the 4-PP. Afterwards a Hall voltage measurement is taken which comprises of a series of voltage measurements with a constant current and a constant magnetic field that is applied perpendicular to the plane of the sample [200]. Once the Hall voltage is found other parameters such as the carrier concentration, carrier mobility, Hall coefficient, magnetoresistance and conductivity type (n- or p-) can be derived. For more detailed information please refer to Ref. [200]. The Hall measurement instrument used in this thesis is an Ecopia HMS-5000 Hall Effect measurement system.

Both the 4-PP and Hall measurements are used throughout this thesis to measure the electrical properties of the various thin films.

## **4.4 Photovoltaic Device Characterisation Tools**

#### 4.4.1 Suns-Voc (Quasi-steady-state Open-circuit Method)

Suns- $V_{OC}$  is a special quasi-steady-state open-circuit method developed by Sinton *et al.* [204] which allows the measurement of the open-circuit voltage,  $V_{OC}$ , of a solar cell without the effect of series resistance. The method works by using a flash lamp with a slow decay that illuminates a separate reference solar cell such that the reference solar cell monitors the change in illumination intensity over time. *Suns-V<sub>OC</sub>* is very similar to the  $J_{SC}$ - $V_{OC}$  [205] measurement except a reference cell in Suns- $V_{OC}$  is used to simultaneously measure the illumination intensity rather than requiring the  $J_{SC}$  of the sample solar cell. Assuming that the short-circuit current density,  $J_{SC}$ , is proportional to the light intensity a pseudo *I-V* curve can be fitted from the data. The *Suns-V\_{OC}* measurement is very useful because solar cells can be measured before metallisation as the results are not affected by series resistance (unless the series resistance is very large). Furthermore, the actual measurement itself is extremely fast and simple.

It is reasonable to analyse  $Sun-V_{OC}$  curves by fitting with a 2-diode model plus a shunt resistance:

$$Suns \cdot J_{SC} = J_L = J'_{01} \left( exp\left(\frac{qV_{OC}}{n_1 kT}\right) - 1 \right) + J'_{02} \left( exp\left(\frac{qV_{OC}}{n_2 kT}\right) - 1 \right) + \frac{V_{OC}}{R_{Shunt}}$$
(4.11)

where the light generated current density,  $J_L$ , is proportional to the "Suns" and  $J_{SC}$  is the short-circuit current at 1-Sun intensity,  $J_{01}$  and  $J_{02}$  are the diode's reverse saturation current densities,  $\frac{kT}{q}$  is the thermal voltage,  $n_1$  and  $n_2$  are diode ideality factors and  $R_{Shunt}$  is the shunt resistance. Using the above equation and examining the diode ideality factors,  $Suns-V_{OC}$  can provide an insight to the type of carrier recombination mechanisms and areas where recombination is occurring. An in-house built  $Suns-V_{OC}$  system is used in Chapter 9 for characterising the superstrate Si QD solar cell devices before and after metallisation.

#### 4.4.2 DarkStar I-V Tester

The most fundamental solar cell characterisation is the measurement of its efficiency. A solar cell simulator with standardised testing conditions is required for this type of characterisation. The in-house built DarkStar *I-V* tester solar simulator is a fully computer-controlled solar cell data acquisition and characterisation system [206]. A typical solar simulator *I-V* tester such as DarkStar consists of a light source close to the standard AM1.5G spectrum (1000W/m<sup>2</sup> for 1-Sun illumination), a temperature stage (with a range from 0 to 100 °C; default 25 °C), measurement electronics and software to generate *I-V* curves. DarkStar uses an Advantest TR6143 DC *V-I* source/monitor for its data acquisition which has computer control functions to automatically sweep the voltage and current.

Dark *I-V* measurements are performed in the absence of light. In the DarkStar *I-V* tester, this is available by covering the sample stage and solar cell under test with a copper casing. Dark *I-V* measurements are usually the first measurements to be performed as they are invaluable in examining diode properties. The current is measured as a function of the swept voltage. In dark *I-V* measurements, carriers are injected into the solar cell as opposed to light generated photocurrent in light *I-V* measurements. In most cases the dark and light *I-V* curves are the same except that the light *I-V* curve is shifted downwards in the graph by the light generated current. I.e. the light *I-V* curve is the superposition of the solar cell diode in the dark (dark *I-V* curve) by the light generated current, *I<sub>L</sub>* [207, 208].

In light *I-V* measurements, the intensity of the light is calibrated by a standard reference solar cell. The illumination intensity is adjusted by the distance between the lamp and the sample stage before the actual measurement. The light *I-V* curve provides the essential solar cell characteristics such as the: open-circuit voltage ( $V_{OC}$ ), short-circuit current ( $I_{SC}$ ), short-circuit current density ( $J_{SC}$ ), max voltage ( $V_{MP}$ ), max current ( $I_{MP}$ ), max power ( $P_{MP}$ ), fill factor (*FF*) and percentage conversion efficiency (*PCE*) usually denoted as  $\eta$  of the solar cell. The light *I-V* characteristics are governed by the following equation [208]:

$$I = I_0 \left( exp\left(\frac{qV}{kT}\right) - 1 \right) - I_L \tag{4.12}$$

where  $I_0$  is the dark saturation current and  $\frac{kT}{q}$  is the thermal voltage. The DarkStar *I-V* tester is used to measure the dark and light *I-V* of the superstrate Si QD solar cell devices in Chapter 8.

# Chapter Five: *In situ* High Resolution Transmission Electron Microscopy of Silicon Nanocrystal Nucleation in a SiO<sub>2</sub> Bilayered Matrix<sup>§</sup>

# **5.1 Introduction**

Tight control over the size, shape and distribution of Si nanocrystals (NCs) or Si quantum dots (QDs) is of great importance in order to realise silicon-based nanostructure tandem solar cells. One of the most common and fundamental characterisation techniques to assess the size, shape and distribution of Si QDs is transmission electron microscopy (TEM) and for the dimensions of our structures specifically high resolution transmission electron microscopy (HRTEM) is required. At present, the nucleation of the Si QDs in the SRO/SiO<sub>2</sub> bilayer matrix configuration requires heating, more commonly referred to as an annealing step. The most common annealing process requires a temperature around 1100 °C and duration of 1 hour in an inert gas atmosphere ( $N_2$  or Ar). This solid-state annealing step takes place below the melting point of both Si (1414 °C) and SiO<sub>2</sub> (1600 °C). Si QDs form during this annealing step and only then can their lattice fringes be seen by TEM. This chapter investigates the growth and nucleation kinetics of Si NCs via in situ annealing using a heating stage accessory inside the chamber of an aberration-corrected FEI Titan 800-300 keV FEG S/TEM. The temperature of the experiment was varied from room temperature up to 600 °C. The work in this chapter was conducted at MIKA, the Electron Microscopy Centre of Materials Science and Engineering Faculty at the Technion – Israel Institute of Technology where the author of the thesis took a student research exchange during the period from mid-November 2012 to late-March 2013.

<sup>&</sup>lt;sup>§</sup> See author's journal publication: T. C. J. Yang, *et al.*, "*In-situ* high resolution transmission electron microscopy observation of silicon nanocrystal nucleation in a SiO<sub>2</sub> bilayered matrix," *Applied Physics Letters*, vol. 105, p. 053116, 2014.

The aim of this study was to examine the nucleation kinetics of Si NCs in real-time. The exact temperature at which nucleation begins to occur in Si NCs embedded in a SiO<sub>2</sub> matrix is not known. This promising in situ experiment reveals the approximate temperature at which the onset of Si NC nucleation occurs for a specific sample, which may be helpful in assessing the method the samples should be annealed with in the future. However, there are differences associated with annealing by a heating accessory inside a TEM chamber compared to conventional furnace or rapid thermal annealing (RTA) procedures, which will be discussed later in this chapter. This experiment also allows the observation of the evolution in the size and structure of the NCs with temperature and time. It is expected that the investigation into HRTEM in situ heating and annealing of Si NCs will also bring additional insights for future experiments in this field of research. Significant time and resources were needed to obtain the results in this chapter as TEM specimen preparation is often challenging as well as time consuming. The first batch of samples prepared for the in situ TEM experiment had nickel contamination in the SRO/SiO<sub>2</sub> layers due to the sputtering from the nickel TEM grids during the ion thinning stage of the preparation and hence are not presented here.

## **5.2 Experimental Details**

Superlattice structures consisting of alternating layers of amorphous SiO<sub>2</sub> (a-SiO<sub>2</sub>) and amorphous SRO (SiO<sub>x</sub>) were deposited via computer-controlled AJA ATC-2200 magnetron sputtering system at room temperature. Radio frequency (RF) power supplies at 13.56 MHz were connected to both a 4 inch SiO<sub>2</sub> and a 4 inch intrinsic Si target. The SRO layers were created by the co-sputtering of both targets, resulting in a sub-oxide, SiO<sub>x</sub> (x < 2), at a combined sputtering rate of 4.87 nm/min. Doping was achieved with RF co-sputtering of a boron (B) 2 inch target for *p*-type doping and phosphine (PH<sub>3</sub>) gas diluted in Ar (99:1) was injected into the sputtering chamber for *n*-type doping. Argon (Ar) was used as the sputtering gas and was introduced into the chamber at 15 sccm with the pressured maintained at 1.5 mTorr. PH<sub>3</sub> at a rate of 3 sccm was used for doping with the Ar rated decreased to 12 sccm in this case.

Single-sided polished *p*-type Czochralski Si (100) wafers (1-10  $\Omega$ cm) were used as substrates for the experiment. The substrates were cleaned in piranha solution (3:1 ratio of H<sub>2</sub>SO<sub>4</sub> to H<sub>2</sub>O<sub>2</sub>) followed by a rinse in deionised water. To remove the native oxide a

diluted 5% HF dip followed by a deionised water rinse and a final  $N_2$  blow dry was performed on the Si substrates prior to placing them in the load-lock chamber of the sputtering system.

The sample consisted of 35 phosphorus (*n*) bilayers: 10 intrinsic (*i*) bilayers, and 25 boron (*p*) bilayers. The sample was similar to the first *p-i-n* structures on quartz presented previously by Perez-Wurfl *et al.* [209], however with different Si content as well as different boron and phosphorus doping concentrations. The SiO<sub>2</sub> thickness was 2 nm and SRO thickness was 4 nm with a Si/SiO<sub>2</sub> volume ratio of 1.92:1. According to the estimated sputter target densities of Si and SiO<sub>2</sub>, the estimated stoichiometry is approximately SiO<sub>0.7</sub>. The deposition rates of the layers were accurately calibrated externally via X-ray reflectivity (XRR) measurements (PANalytical X'Pert Pro MRD) and spectroscopic ellipsometry (J.A. Woollam Co. M-2000). The stoichiometry of the SRO layer could be accurately controlled by adjusting the power of the Si and SiO<sub>2</sub> targets. A final 20 nm SiO<sub>2</sub> capping layer was deposited to avoid unwanted oxidation through the top surface both during the standby and annealing stages.

The sample for TEM analysis was prepared by focused ion beam (FIB) slicing, producing small lamellas on a titanium grid holder. Gentle  $Ar^+$  milling was performed on both the top and bottom sides of the specimen at an angle between 12° and 15° using a Technoorg LINDA, Gentle Mill, IV8 system (to allow for further thinning below 100 nm) prior to TEM observation. The *in situ* heating experiments were conducted in a Titan 80-300 S/TEM (FEI) equipped with a spherical aberration (C<sub>s</sub>) corrector for the objective lens, operated at an accelerating voltage of 300 kV. The TEM specimens were mounted on a Gatan 652 double-tilt heating holder stabilized by active water cooling when used at temperatures above 500 °C. A maximum temperature of 950 °C can be achieved by this system, but in this work the temperature did not exceed 600 °C.

# 5.3 Results and Discussion

Figure 5.1 shows a bright-field TEM micrograph of as-deposited *n*-type phosphorous doped SRO/SiO<sub>2</sub> bilayers of the *p-i-n* stack. The substrate at the top of the image is crystalline Si (c-Si). Note that when deposited, the thickness of the amorphous SRO

(darker) and SiO<sub>2</sub> (lighter) layers were 4 nm and 2 nm respectively. These values were calculated from accurate XRR and spectroscopic ellipsometry measurements. However, from the TEM micrograph, the SiO<sub>2</sub> layers appear thicker and the SRO layers slightly thinner than expected. According to measurements performed on the digital micrographs using the software ImageJ, the SiO<sub>2</sub> layers are 2.3-2.4 nm and the SRO layer thickness between 3.7 and 3.8 nm. A possible explanation to the apparent change in thickness may be stress induced across the SiO<sub>2</sub>/SRO interface due to preferential growth of the oxide nucleus in the vertical direction during pre-imaging preparation steps and/or due to long term standby in air. Nevertheless, the total thickness of 10 bilayers is 61 nm, which gives an average thickness of 6.1 nm for a single bilayer which was consistent within the measurement error for the original calculated sputter deposition rate.





In TEM imaging of amorphous materials, contrast arises due to the differences in atomic number and density of the materials as well as the thickness of the specimen. In general, the denser or thicker the material, the darker the region will be due to increased scattering of the incident electrons. However at high magnifications, such as Figure 5.2 and Figure 5.5, complex wave interactions modulate the intensity of the image, requiring further analysis. There has been ongoing discussion on the ability of HRTEM to resolve amorphous structures [210]. The resolution of HRTEM is constrained most heavily by spherical aberration of the objective lens,  $C_s$ , which delocalise the contrast of a point object. The Titan S/TEM system which is equipped with  $C_s$  correction has a best point resolution of 0.07 nm. Therefore it has the ability to image individual columns of atoms in c-Si. In general, however, when imaging Si NCs. The image contrast of the NCs are superimposed onto that of the surrounding amorphous matrix and this leads to slight loss in detail [211]. Hence, the specimen must be prepared additionally thin when viewing NCs in an amorphous matrix to reduce the fraction of amorphous material being imaged. In this study, the sample thickness in all images was below 80 nm. Specimen thicknesses can be measured accurately using electron energy loss spectroscopy (EELS). When the electron beam penetrates a thin specimen with thickness, *t*, the fraction of inelastic scattering will depend on the density and thickness by the log-ratio equation [212]:

$$\frac{t}{\lambda} = \ln\left(\frac{I_T}{I_{ZLP}}\right) \tag{5.1}$$

Where  $\lambda$  is the electron mean free path for inelastic scattering,  $I_T$  is the total integrated area under the EELS spectrum and  $I_{ZLP}$  is the total area under the zero-loss peak. The electron mean free path was determined previously for Si at 199 ± 20 nm and amorphous SiO<sub>2</sub> at 238 ± 12 nm by the microscopy experts at the Technion – Israel Institute of Technology where this experiment was conducted [213]. The experimental values of the electron mean free path that the authors obtained underestimates the true sample thickness for high accelerating voltages (300 kV) and at large collection angles.



Figure 5.2. In situ HRTEM micrograph of the p-i-n specimen at 400 °C.

From Figure 5.1, the temperature was gradually increased to 400 °C over a period of 30-45 min and allowed to stabilise before the image was captured at a higher magnification shown in Figure 5.2. There was drift associated with the expansion and contraction of the heating stage that may have contributed to a decrease in resolution. Note the [200] arrow in Figure 5.2 points into the Si (100) substrate and the direction looking perpendicular into the page (i.e. the normal to the page) is the Si (111) plane, which is the plane that the electron beam is aligned to. The diamond-cubic Si (111) plane arrangement is recognized by the typical 70.5° angle between the two main crisscrossing planes, and a lattice separation of 3.1 Å which is typical for diamond-cubic Si. When analysing lattices images however, caution should be exercised due to the fact that the observed images do not necessarily reflect the atomic arrangement. What the observers sees is actually an image which is the deconvolution of the difference in the amplitude of the electron wave functions from interference of the transmitted and diffracted beams.



Figure 5.3. In situ HRTEM micrograph of the p-i-n specimen at 450 °C.

From Figure 5.2 to Figure 5.3, the contrast between the SRO and SiO<sub>2</sub> layers seems to decrease as the temperature is increased to 400 °C. This may indicate that the density of the SRO is becoming closer to that of the SiO<sub>2</sub>, although the defocus conditions may have some effect on this (see below for explanation). This result may be attributed to the phase separation and rearrangements of the Si and SiO<sub>2</sub> in the SRO layers. More importantly, this may be an indicator to the pre-nucleation or onset of nucleation stage. The phase separation is governed by the following reaction:

$$SiO_x \longrightarrow \frac{x}{2}SiO_2 + \left(1 + \frac{x}{2}\right)Si$$
 (5.2)

In Figure 5.3, the nucleation of the Si NCs has occurred, with lattices visible (circled). However, not all existing Si NCs can be seen, because the lattice planes will only be visible when they are oriented in the same way as the substrate orientation, as the electron beam is aligned to the substrate zone axis [18, 211, 214, 215], in this case, the c-

Si (111) plane. Hence, only those Si NCs that are orientated in the Si (111) alignment with a lattice separation of 3.1 Å are visible. Furthermore, there is a phenomenon that the lattice fringes of Si NCs can only be seen if the specimen is either slightly over-focused or under-focused [211]. If the specimen is completely in focus,  $\Delta f = 0$  nm, then the contrast between the Si NCs and the background amorphous matrix disappears. A defocused set of images would better differentiate the regions of crystallinity with the background amorphous film. An estimate for reasonable values of the focus setting in this case would be  $\Delta f = \langle \pm 20 \text{ nm}, \text{ according to a few sources } [211, 214, 216-218]$ . Taking this limitation into consideration, the total proportion of the Si NCs in the SRO layers is actually much higher than the visible nanocrystalline areas in the images, as shown by Yurtsever et al. [55] through direct comparison of TEM and plasmon tomography. In addition, the true size and shape of the individual NCs is difficult to discern from 2D TEM images alone because limited information is given along the third dimension (depth) and what we really observed is the average along the specimen. This means that along the depth there could be overlaps of isolated NCs or complex networks, making the exact morphology difficult to determine. This has been an ongoing discussion in several past publications [55, 56, 59].



Figure 5.4. In situ HRTEM micrograph of the *p-i-n* sample after 15 min at 500 °C.

The sudden nucleation of the Si NCs at a relatively low temperature of 450 °C was rather peculiar. Most centres around the world involved in this research have used much higher annealing temperatures to grow Si NCs in an oxide [18, 53, 60, 218-221]. There are some significant advantages of lower nucleation temperatures, such as lower cost in manufacturing or compatibility with other materials, for example, glass substrates and transparent conducting oxide electrodes. There are a few plausible explanations for this unexpected phenomenon:

- The Si content of the SRO layers was relatively high compared to most other samples to the point that the SRO layer may behave more like a quantum-well type of structure. The distance for diffusion Si atoms is therefore decreased for higher Si content SRO.
- 2) The specimen thickness was well below 80 nm (measured with EELS). Therefore, the properties may deviate from thicker films.
- The *in situ* annealing experiment was conducted under vacuum conditions; in almost all other cases, an inert gas (Ar or N<sub>2</sub>) was used during furnace annealing at atmospheric pressure
- 4) High-electron beam accelerating voltages may have been an additional source of energy, resulting in lower activation energy for the nucleation process to occur [216, 222, 223] (this is sometimes a problem with conventional TEM imaging of sensitive materials) It was brought to recent attention work from Stevens-Kalceff [224] which demonstrated the radiolytic properties and sensitivity of SiO<sub>2</sub> under electron irradiation through cathodoluminescence. The results showed the radiolytic production of interstitial oxygen molecules in oxygen deficient and stoichiometric SiO<sub>2</sub> polymorphs under electron beam energies well below the minimum for knockon (momentum transfer) to occur.
- 5) Preparation damage from either the impact of the Ga<sup>+</sup> ions in the FIB or Ar milling may have altered the surfaces prior to observations. E.g. further amorphisation or mixing of the SRO and SiO<sub>2</sub> layers.



**Figure 5.5.** *In situ* HRTEM micrograph of the *p-i-n* sample after 40 min at 500 °C and 10 min at 600 °C.

There were no significant visible changes between Figure 5.4 and Figure 5.5 after 40 min at 500 °C and 10 min at 600 °C, which may indicate that the nucleation has stabilised. In general, Si QDs in HRTEM usually appear spherical according to most sources [18, 51, 53, 60, 225-227]; however, the images seen in this *in situ* HRTEM experiment seem to be of an irregular nature. Although the shape is difficult to discern in 2D HRTEM, we observed roughly an aspect ratio of over 2:1 for some of the Si NCs. Previous X-ray diffraction (XRD) measurements by Di *et al.* [228] on moderate content, 1.24:1 volume ratio, Si/SiO<sub>2</sub> samples suggest a NC line size greater than 10 nm, but do not address the actual shape. Furthermore, it was suggested that the Si NCs were "physically penetrating three thin layers" in the vertical direction across adjacent SiO<sub>2</sub> layers. However, in all of the figures in this chapter, this does not seem to be the case. Instead, the Si NCs are well confined consistently within each layer, even for thin 2 nm SiO<sub>2</sub> barrier layers. The irregular/elongated shape however may affect the quantum confinement of excitons due to higher interface defect densities as the surface area-to-volume ratio increases when the

shape digresses from the ideal QD sphere, at least for QDs with the same number of Si atoms. Yurtsever *et al.* [55] also show that the dominant morphology of Si NCs is indeed irregular and complex rather than the commonly assumed near-spherical structures. These findings may provide an explanation for the broad photoluminescence spectra characteristic of Si NCs formed by solid phase crystallisation [229]. With further analysis some percolation threshold may also be established in these Si NC films.

# **5.4 Conclusion**

This experimental study illustrates the utility of spherical aberration corrected HRTEM with real-time in situ heating on the nucleation of Si NCs in an amorphous SiO<sub>2</sub> bilayered matrix. Low temperature nucleation was observed beginning already at 450 °C, however there are differences between *in situ* annealing inside a TEM compared to conventional ex situ annealing methods as discussed above. If this unexpected low temperature nucleation of the Si NCs was indeed true, other materials that would otherwise not survive the standard high temperature (1100 °C) annealing stage could be incorporated in the device design of Si QD solar cells, such as low melting point transparent conducting oxides for example. In future, a comparison between in situ HRTEM annealing and ex situ annealed specimens would be beneficial to further understanding the solid-state nucleation kinetics of Si QDs in an amorphous SiO<sub>2</sub> bilayered matrix. Unfortunately due to time and resource constraints a direct comparison between in situ and ex situ annealed specimens could not be conducted during the author's time at the Technion – Israel Institute of Technology. The shape and morphology of the Si NCs appears to be highly irregular which may possibly be due to the high Si content that was used. However, the Si NCs were well confined within their own SRO layers. Other techniques such as Rutherford back-scattering spectroscopy (RBS), atom probe tomography (APT), plasmon tomography and/or 3D HRTEM may need to be investigated to obtain a better understanding to the size, shape and proportion of the silicon NCs. A more careful analysis of the actual annealing temperature for ex situ annealed SRO/SiO<sub>2</sub> bilayer can be found in the next chapter.

# Chapter Six: Study of High Silicon Content SRO/SiO<sub>2</sub> Bilayer Superlattice Thin Films with Boron and Phosphorus Doping<sup>\*\*</sup>

# **6.1 Introduction**

The Si QDs studied in this chapter were fabricated by magnetron sputtering Si rich oxide/S dioxide (SRO/SiO<sub>2</sub>) bilayer thin film superlattices followed by high temperature annealing. This chapter investigates the use of high Si content in the SRO layers with advantages such as lower resistivity and higher absorption cross-sections which are more suitable for photovoltaic devices. A possible drawback however is that higher Si content SRO seems to produce greater size distribution and larger Si NCs, theoretically lowering the bandgap towards that of crystalline Si (c-Si). For these reasons, it seems that many researchers have been hesitant to pursue this path.

This chapter also investigates the dependence of annealing temperature on the Si NC formation using both grazing incidence X-ray diffraction (GIXRD) and Raman spectroscopy as the previous chapter on *in situ* temperature annealing high resolution transmission electron microscopy (HRTEM) [230] and elsewhere [56] have suggested that the *ex situ* furnace annealing nucleation temperature may not need to be as high as the 1100 °C which is the temperature that most previous studies have used.

Impurity doping of Si QDs is still not well understood as the doping mechanism is more complex than in c-Si [63]. Nevertheless to create solar cell devices, a selective doping mechanism for carrier separation is required. This could either mean a *p-n* or a *p-i-n* junction. Boron (B) and phosphorus (P) are the most common dopants in the photovoltaics industry today for c-Si solar cells due to their high solid solubility in Si and their reasonable diffusion rates that make junction depths easily controllable. Therefore, doping with B or P

<sup>&</sup>lt;sup>\*\*</sup> See author's conference proceeding: T. C.–J. Yang *et al.,* "High Si Content SRO/SiO<sub>2</sub> Bilayer Superlattices with Boron and Phosphorus Doping for Next Generation Si QD Photovoltaics" in *42<sup>nd</sup> IEEE Photovoltaic Specialists Conference (PVSC)*, New Orleans, LA, United States, 2015, pp. 1-6.

is also studied in this chapter as they alter the structural, optical and electrical properties of these SRO/SiO<sub>2</sub> superlattice thin films. Previous investigation on the doping of Si QDs in more moderate Si content SRO/SiO<sub>2</sub> bilayer thin films have shown effective doping of both B and P for *p*-type [70] and *n*-type [71] respectively. A general decrease in resistivity of many orders of magnitude accompanies the doping of the Si QD superlattice structures. Current crowding and high series resistance were encountered for *p-i-n* Si QD solar cell devices with an open-circuit voltage of 493 mV, fabricated by Perez-Wurfl *et al.* [209, 231]. Recent efforts in Si QD solar cell devices have focused on higher Si content SRO to avoid current crowding and to decrease series resistance [232]. It has been suggested that higher Si content SRO tends to make better solar cell devices due to both their lower resistivity [77] and higher light absorption cross-sections [63]. The work in this chapter may be beneficial for future researchers in the area of solid-state Si QDs for third generation photovoltaics.

## **6.2 Experimental Details**

Bilayers of SRO/SiO<sub>2</sub> were deposited via a computer-controlled AJA ATC-2200 magnetron sputtering system at room temperature. Radio frequency (RF) power supplies (13.56 MHz) were connected to a 4 inch intrinsic Si and 4 inch SiO<sub>2</sub> target. Doping was achieved via co-sputtering with either a 2 inch B or 2 inch  $P_2O_5$  target. Argon was injected into the chamber at a rate of 15 sccm with the chamber pressure maintained at 1.5 mTorr.

Both fused quartz and single-side polished *p*-type Czochralski Si (100) wafers (1-10  $\Omega$ cm) were used as substrates. The substrates were piranha cleaned and then rinsed in deionized water. Additionally, the Si wafers were dipped in 5% HF solution to remove the native oxide prior to deposition.

There were 3 depositions with 3 sample sets. Each set of samples consisted of 30 bilayers of 4 nm thick SRO and 1.8 nm of SiO<sub>2</sub>. A final 20 nm SiO<sub>2</sub> capping layer was deposited to protect the film from oxidation and contamination during standby and annealing stages. The RF power to the Si and the SiO<sub>2</sub> targets were 264 W and 120 W respectively with a combined deposition rate of 4.74 nm/min. The resultant volume ratio of Si:SiO<sub>2</sub> was approximately 7:3. The deposition rates were calculated *ex situ* via spectroscopic ellipsometry. According to the estimated sputtered target densities of the Si and SiO<sub>2</sub> thin

films, the calculated stoichiometry is approximately  $SiO_{0.3}$ . In the first deposition there was no doping (intrinsic samples). For the second and third deposition, B and  $P_2O_5$  targets were co-sputtered in the SRO layers with a target power of 25 W each. There was no measureable change in the deposition rate with the addition of the B and  $P_2O_5$  targets during the co-sputtering as their rates were almost insignificant compared to the rates of the Si and SiO<sub>2</sub>.

Finally, all samples were annealed individually in a 1 L volume conventional quartz-tube furnace at various temperatures up to 1100 °C with a nitrogen ( $N_2$ ) flow of 2.5 L/min for 1 hour to allow the Si NCs to form in the SRO layers. The samples were then analysed by grazing incidence X-ray diffraction (GIXRD), high resolution transmission electron microscopy (HRTEM), Raman spectroscopy and photoluminescence (PL) spectroscopy. Several basic electrical measurements were also conducted. The 20 nm SiO<sub>2</sub> cap was removed by dipping in 5% HF solution for 90 seconds before the electrical measurements.

# 6.3 Results and Discussion

## 6.3.1 Grazing Incidence X-Ray Diffraction

The GIXRD system (PANalytical X'Pert Pro MRD) with Cu  $K\alpha$  radiation ( $\lambda = 0.1542$  nm) was operated at a voltage of 45 kV and a current of 40 mA. The grazing angle between the thin film surface and the X-ray beam was set at 0.27° which is close to the critical angle. The primary optics consisted of a 1/16° divergence slit in front of a parabolic mirror. The secondary optics consisted of a parallel plate collimator with an acceptance angle of 0.27° and a 0.04 radian aperture Soller slit.





**Figure 6.1.** GIXRD patterns of (a) intrinsic, (b) boron and (c) phosphorus doped high Si content SRO/SiO<sub>2</sub> bilayered thin films on quartz substrates annealed at various temperatures for 1 hour in a 1 L quartz tube furnace with a  $N_2$  flow rate of 2.5 L/min.

Figure 6.1 shows the GIXRD patterns of (a) intrinsic, (b) boron and (c) phosphorus doped high Si content SRO/SiO<sub>2</sub> bilayered thin films on quartz substrates which were annealed at various temperatures up to 1100 °C for 1 hour in a 1 L quartz tube furnace with a N2 flow rate of 2.5 L/min. There is a distinct broad peak at 21.0° which is characteristic of the amorphous SiO<sub>2</sub> (a-SiO<sub>2</sub>) phase for all samples. For the 3 types of samples other peaks associated with Si NC formation (which are described in more detail in the next paragraph) can be observed clearly when annealed at 1100 °C. In some cases a less distinct peak was observed at 1000 °C. At 1000 °C the P doped sample (Figure 6.1(c)) seems to show slightly larger and sharper peaks than the intrinsic, (Figure 6.1(a)) and B doped (Figure 6.19(b)) samples. For annealing temperatures 800 °C and below there are no observable peaks other than the broad a-SiO<sub>2</sub> peak at 21.0° for all samples. The temperature dependence results for the GIXRD suggests that conventional furnace annealing requires temperatures of at least 1100 °C for satisfactory Si NC formation, which is contrary to the hypothesis in the last chapter when the in situ HRTEM experiment suggested that Si NC nucleation may start at a low 450 °C. Although, it is worth mentioning that GIXRD will require a significantly higher density of crystals to detect their presence compared to HRTEM.



**Figure 6.2.** GIXRD patterns of the 1100 °C annealed intrinsic, B and P doped SRO/SiO2 bilayer thin films on quartz substrates (a) full range and (b) with a separate higher resolution scan near range of the Si(111) peaks.

Figure 6.2(a) compares the GIXRD patterns of the annealed intrinsic, B and P doped  $SRO/SiO_2$  bilayered thin film samples. For all three diffraction patterns four distinct peaks are visible at 21.0°, 28.5°, 47.4° and 56.4°. The wide peak at 21.0° is characteristic of the a-SiO<sub>2</sub> phase as stated before and the latter three peaks are near the expected Bragg peaks of Si(111), Si(220) and Si(311) respectively. These strong peaks are indicative of Si NC formation in the thin films.

In terms of the size effect that the dopants have on the Si QDs, there are some inconsistencies between reports on B doping with some sources reporting no change and some reporting of a decrease in the size. However the size seems to increase with P doping in most reports. TEM, XRD and Raman data from Hao *et al.* [70] seem to suggest that the size of the QD does not change with increasing B concentration but the crystalline volume percentage in the film decreases. This is consistent with a few references where

chemical vapour deposition is used to fabricate the Si thin films that indicate that B suppresses Si nucleation [233, 234]. The size of the Si NCs in this experiment were estimated using the Scherrer equation using the Si(111) peak 28.5° and a shape factor, Kof 0.9 [189] from the high resolution scans in Figure 6.2(b). The Scherrer broadening equation estimates the dimension of columns of cubic cells aligned perpendicularly to the set of diffraction planes and gives the minimum size of the crystallite. The estimated average size for the Si NCs in the intrinsic, B and P doped samples are  $9.1 \pm 2.4$  nm,  $9.6 \pm$ 2.0 nm and 11.1 ± 2.2 nm respectively. The large estimation error is due to the difficulty in gauging the full width at half maximum (FWHM) of the Si(111) peaks as they are masked by the stronger and broader a-SiO<sub>2</sub> peak at 21.0°. Even though the Scherrer equation is often used to measure the size of Si NCs, it does not clearly provide an indication of the shape or the size distribution of the NCs. If the bold assumption is that the Si NCs are indeed spherical, then the average volume of the Si NCs in the intrinsic, B and P samples are approximately 400, 460 and 720 nm<sup>3</sup> respectively. And given that bulk c-Si has a density of  $5 \times 10^{22}$  atoms/cm<sup>3</sup> or approximately 50 atoms/nm<sup>3</sup>, the number of atoms per Si NC in the intrinsic, B and P samples would be around 20000, 23000 and 36000 respectively. Table 6.1 provides a summary of the GIXRD results.

Table 6.1. GIXRD	Si NC size and vo	lume estimates

	Intrinsic	Boron	Phosphorus
Average diameter (nm)	9.1 ± 2.4	9.6 ± 2.0	11.1 ± 2.2
Average volume (nm <sup>3</sup> )	400	460	720
Average number of atoms per NC	20000	23000	36000

The next subsection on HRTEM and energy-filtered transmission electron microscopy (EFTEM) provide a clearer examination of the extent of crystallization in these high Si content SRO/SiO<sub>2</sub> bilayered films.

## 6.3.2 High Resolution and Energy Filtered Transmission Electron Microscopy

The HRTEM images were taken with a JEOL 2200FS operated at an accelerating voltage of 200 kV. The specimens were prepared by conventional mechanical thinning methods. EFTEM was employed to provide a clearer contrast between the Si and  $a-SiO_2$  regions.



**Figure 6.3.** (a) Bright-field HRTEM and (b) corresponding EFTEM image of annealed intrinsic SRO/SiO2 bilayers under a magnification of 800,000×.

Figure 6.3(a) shows a HRTEM image of the annealed intrinsic SRO/SiO<sub>2</sub> bilayered sample under 800,000× magnification. There is a clear distinction between the SRO and SiO<sub>2</sub> layers because lattice fringes, indicative of Si NC formation are clearly visible in the SRO layers. The measured lattice spacing is approximately 3.1 Å which is typical of diamondcubic Si. Note however, not all the existing Si NCs in the SRO layers can be seen in HRTEM, only those that are orientated in the same way as the substrate orientation (diamond-cubic Si(111) plane) are actually visible [18, 211, 214, 215] (or see Chapter 5). Figure 6.3(b) shows the corresponding EFTEM image. EFTEM is often used for elemental mapping as it provides higher lateral resolution than conventional bright-field TEM. The EFTEM imaging was tuned to the value of 17 eV for the Si bulk plasmon and 23 eV for the SiO<sub>2</sub> bulk plasmon signal with an energy window of 4 eV. The contrast between the Si and the a-SiO<sub>2</sub> is clearly enhanced from Figure 6.3(a) to (b). Furthermore, given that higher amounts of Si tend to be found in Si NCs the location of the Si NCs also appear more intense and is also independent of the actual Si NC orientation.



**Figure 6.4.** (a) Bright-field HRTEM and (b) corresponding EFTEM image of annealed B doped SRO/SiO<sub>2</sub> bilayers under a magnification of  $500,000 \times$ .

The Si NCs in Figure 6.3 mostly form exclusively within the SRO layers. However in Figure 6.4 where B is doped in the SRO layers during the sputtering, there does not seem to be any distinction between the SRO/SiO<sub>2</sub> bilayers. After the high temperature anneal at 1100 °C, Si crystallisation has occurred across multiple layers. This shows that the 1.8 nm SiO<sub>2</sub> layers are insufficient to physically confine the Si NCs. The most likely reason is the softening of the matrix as seen by Fuiji *et al.* [73]. Although this may seem discouraging at first, it may not actually imply that the quantum confinement is necessarily compromised (see section on PL). Even though there are some areas in Figure 6.4 with extensive Si crystallisation, there are still large areas of a-SiO<sub>2</sub> or possibly a sub-oxide (SiO<sub>x</sub>).



**Figure 6.5.** (a) Bright-field HRTEM and (b) corresponding EFTEM image of annealed P doped SRO/SiO<sub>2</sub> bilayers under a magnification of  $500,000 \times$ .

The structural morphology in Figure 6.5 is similar to Figure 6.4 in that the bilayer formation is lost. However, it can be deduced that from Figure 6.5(b) the Si crystallisation is even more extensive as there are fewer areas of a-SiO<sub>2</sub> regions and brighter Si NCs regions in the EFTEM image (i.e. higher contrast). This result for the P doped sample is consistent with previous studies on P doping of Si NCs, which strongly suggest that P assists in the crystallisation of Si NCs [71].

Although it is difficult to digitally estimate the average size of the Si NCs due to their irregular shape and wide size distribution, from the EFTEM image, the observable crystallisation is fairly extensive as most of the NCs are already wider than the 5 nm scale bar. Overall the Si NC size assessment from HRTEM and EFTEM correlate well with the GIXRD Scherrer equation estimates. Most previous HRTEM and EFTEM studies on lower Si content SRO have shown or suggested that the shape of the Si NCs as near spherical [18, 51, 53, 60, 225, 226], but this is not the case in this experiment as the average size for all three samples obtained from GIXRD are all greater than the thickness of the SRO layers which were only 4 nm before the high temperature anneal. The arbitrary shape is more likely due to the high amount of Si that is used in the SRO layers which probably exceeds a threshold for spherical nanocrystallisation. This could either mean that the Si NCs are penetrating through the adjacent 1.8 nm SiO<sub>2</sub> layers as suggested by Di *et al.* 

[228] or there could be an extensive nanocrystalline Si network [235] within the SRO layers making the Si NCs non-spherical in shape. Furthermore, if the Si NCs are confined well within the layers, Si quantum well structures could also be a possibility. In HRTEM it is often difficult to find the true shape of the individual Si NCs, because limited information is given to the viewer along the third dimension (depth) [55].

The shape has been suggested to be elliptical or even more eccentric as suggested by a few TEM based studies in the past [55-57, 59, 215]. In reality, Si NCs which initially begin as small spherical NCs will over time most likely combine with neighbouring Si NCs. The probability of this occurring is even greater in this case as the Si content in the SRO is much higher than most previous studies. An interpenetrating Si nanocrystalline network may actually assist in carrier transport. In addition, smaller surface area to volume ratio between the Si NCs and the a-SiO<sub>2</sub> matrix could result in less defects and better electronic quality.

#### 6.3.3 Raman Spectroscopy

Raman measurements were taken at room temperature with an inVia (Renshaw) confocal microscope system. A green 514.4 nm wavelength Ar<sup>+</sup> laser was used as the excitation source.





**Figure 6.6.** Absolute Raman spectra of the (a) intrinsic, (b) B and (c) P doped SRO/SiO<sub>2</sub> bilayers on quartz substrates with annealing temperature up to 1100 °C. A normalised c-Si reference from a c-Si wafer is included as a guide.

First order Raman spectra can easily determine whether a Si thin film is amorphous, crystalline or a combination of both. Raman spectroscopy measurements for intrinsic, B and P doped SRO/SiO<sub>2</sub> bilayer samples from Figure 6.6(a)-(c) show sharp peaks near a Raman shift of 519 cm<sup>-1</sup> (i.e. c-Si Ref.) for samples annealed at 1000 °C and 1100 °C which is indicative of c-Si due to the conservation of the characteristic optical phonon

momentum. A broad peak around the 480 cm<sup>-1</sup> region is attributed to the amorphous Si (a-Si) component. The formation of Si NCs can be easily seen by the evolution of the Raman spectra as the annealing temperature increases. The ratio between the area under the broad a-Si peak and the sharp c-Si peak decreases sharply from an annealing temperature of 800 °C to 1000 °C signifying some type of activation energy that is required for the nucleation and formation of the Si NCs.



**Figure 6.7.** (a) Normalized Raman spectra of the annealed intrinsic, B and P doped  $SRO/SiO_2$  bilayers on quartz substrates as well as the spectrum from a reference c-Si wafer. (b) Example of the peak fitting for the B doped sample.

Figure 6.7(a) gives a clearer comparison between the intrinsic, B and P doped samples that were annealed at 1100 °C. The Raman peaks were deconvoluted into crystalline and amorphous components using the software package OriginPro 2015. An example of the peak fitting for the B sample is shown in Figure 6.7(b). Gaussian components were used to fit the broad amorphous peak at 480 cm<sup>-1</sup> and Lorentzian components for the c-Si peak around 519 cm<sup>-1</sup>. For the intrinsic and B spectra, an additional small Lorentzian peak at 512.4 cm<sup>-1</sup> was required for the fitting. This peak is related to grain boundary interface between the Si NCs and the surrounding a-SiO<sub>2</sub> matrix [236, 237]. The integrated intensities of the crystalline (*I<sub>c</sub>*) and amorphous (*I<sub>a</sub>*) peaks were calculated and using the quantitative model proposed by Tsu *et al.* [238] an estimate for the fraction of Si that is
crystalline can be obtained. The corrected equation for the crystalline fraction is shown below:

$$x_c = \frac{x_{nc}}{x_{nc} + y \cdot (1 - x_{nc})}$$
(6.1)

where  $x_{nc} = \frac{l_c}{(l_c+l_a)}$  and  $y = \frac{\Sigma_c}{\Sigma_a}$  is the integrated Raman cross-section for c-Si to a-Si, which is usually between 0.8-0.9 as calculated from previous studies. The calculated crystalline fraction for the intrinsic, B and P doped samples are 0.65, 0.68 and 0.73 respectively. The calculation for the crystalline fraction using (6.1) above has been used in many studies for c-Si/a-Si mixture films. However, there are variations to equation (6.1) as well as the analysis of the Raman spectra between studies making cross-comparison of the absolute quantification of the crystalline fraction unreliable and should be done so with caution. Although generally within each study, the relative crystalline fraction between different samples seems consistent. In general for this analysis the crystalline fractions are relatively high compared to other studies as a result of higher Si content used overall as well as the high annealing temperature at 1100 °C. The analysis from Raman within this study agrees well with both the GIXRD and HRTEM results above.

#### 6.3.4 Photoluminescence

The PL measurements were taken using an in-house built system with a 405 nm diode laser as the excitation source. The luminescence signal was collected by a multi-channel Si CCD thermoelectrically cooled to -30 °C for noise reduction.



**Figure 6.8.** Normalized RT PL spectra of the intrinsic, B and P doped SRO/SiO2 bilayer samples on quartz substrates.

Figure 6.8 shows the normalized room temperature (RT) PL spectra of the three samples. There is a distinct red-shift from 840 nm (1.48 eV) to 940 nm (1.32 eV) when the SRO was doped with P, however there was no evidence of a significant change when doped with B. The quantum confinement model predicts a blue-shift in the PL spectrum with decreasing Si QD size which corresponds well with the increase in size of the Si NCs with P doping from GIXRD, however there is no shift for B doping, even though the GIXRD predicts a slightly larger NC size for B compared to the intrinsic case. Quenching and a slight blueshift in the PL with the addition of B have suggested indirectly that the size and number of Si NCs decreases with B doping [67, 72], although the effect of using higher Si content in the SRO resulting in larger Si NCs may have cancelled out this effect. It is also possible that there are smaller Si NCs left in the B doped sample which dominate the PL emission, particularly if B doping adds non-radiative defects to the larger NCs. On the other hand the size enhancement effect was also shown indirectly through the red-shift observed via PL when Si NCs are doped with phosphorus [67] which is consistent with these results. The PL intensity of the P doped sample before normlisation is about 4.5 times greater than both the intrinsic and B samples (which both had about the same absolute intensity). This again confirms the larger NC size and the higher crystalline to amorphous fraction of the P doped sample as the absorption capture cross-section for the PL laser is greater for larger Si NCs. It may also indicate that P improves the radiative recombination of crystals.

#### **6.3.5 Electrical Measurements**

	R <sub>sheet</sub> (kΩ/□)	R <sub>bulk</sub> (Ωcm)	Mobility, µ (cm²/Vs)	Carrier Concentration (cm <sup>-3</sup> )
B (4-PP)	43	0.75	-	-
P (4-PP)	6200	106	-	-
B (Hall)	41	0.66	0.36	+2.6 ×10 <sup>19</sup>
P (Hall)	7700	120	0.24	-2.2 ×10 <sup>17</sup>

Table 6.2. 4-PP and Hall measurements

Table 1 shows the four-point probe (4-PP) and Hall measurements for the B and P doped samples on insulating quartz substrates. Due to the high doping concentrations of B and P, the samples showed near ohmic properties with the Hall contacts. The intrinsic sample was not able to be measured by these two techniques because the resistivity is many orders of magnitudes higher than the doped samples [70, 71]. For the 25 W sputter power used, B samples have a very low resistivity of 0.66 Ωcm from Hall measurements. The hole concentration is 2.6  $\times$  10<sup>19</sup> cm<sup>-3</sup> which is similar to films measured in the past by capacitance-voltage measurements on inverted metal-oxide-semiconductor devices [239]. The resistivity (120  $\Omega$ cm) and carrier concentration (2.2 × 10<sup>19</sup> cm<sup>-3</sup>) of the P doped sample are higher than those of the B doped samples. This is surprising because a higher c-Si fraction should theoretically allow higher doping efficiency as well as better current transport. A possible explanation could be an over-doping of P as seen in the study by Hao et al. [71]. Their study suggested aggregation or clumping of inactive P atoms as well as compromise to the crystallinity of the films. A more likely scenario is the fact that P causes larger Si NCs, but also increases the inter-NC spacing as evident to some extent from the EFTEM images. The carrier mobilities of both samples are still much lower than carrier mobilities in degenerately doped c-Si. The low mobility is expected given the nature of the transport mechanisms in these types of materials. Previous electrical measurements by other authors on similar SRO/SiO<sub>2</sub> superlattice thin films showed a large change in resistivity for a small change in dopant concentration [70, 71, 240]. It has been suggested that using phosphine gas instead of co-sputtering P<sub>2</sub>O<sub>5</sub> for doping may be better due to phosphine's ability to reduce defects [241].

It was shown from the Section 2.7 of Chapter 2 that there is evidence to show effective doping of these  $SRO/SiO_2$  films. However, the exact doping characteristics of these Si NCs are still not well understood. The three regions of interest are dopants:

- 1) Inside the Si NCs.
- 2) In the SiO shell surrounding the Si NCs.
- 3) In the SiO<sub>2</sub> matrix

The hypotheses and discussion as to the real nature of doping are explained below. Recent atom probe tomography (APT) [242] using proxigram analysis has shown that approximately 15% of the P atoms are found inside the Si NCs, 30% in the interface and 55% in the SiO<sub>2</sub> matrix. The relatively low value inside the Si NCs has already been explained by the self-purification mechanism (see Section 2.6 of Chapter 2). More recent work by König et al. [243] (2015) has shown that nearly all the 15% P atoms reside as interstitial rather than substitutional impurities. However neither interstitial nor substitutional impurities (which provide defect levels) are likely to contribute to free carriers at RT simply because their ionisation energies are still too high. This effect should be similarly for P atoms in the SiO shell surrounding the Si NCs although the deep defects should not be as deep. Furthermore, in this experiment, the ionisation energies decrease especially with larger Si NCs. The EFTEM images seem to suggest that the SiO shell extends further for B doped compared to P doped samples as the contrast change is higher from Si NC to the SiO<sub>2</sub> matrix from Figure 6.5(b) to Figure 6.4(b). Further density functional theory (DFT) calculations show that P dopants in the SiO<sub>2</sub> matrix actually reduce the transport barriers for electrons and holes by 97% and 85% respectively [243]. This would cause a substantial increase in conductivity although the P is strictly not acting as a dopant.

## 6.4 Conclusion

High Si content SRO/SiO<sub>2</sub> bilayer superlattice thin films were fabricated via RF magnetron sputtering. The approximate stoichiometry of the SRO layers was SiO<sub>0.3</sub>. B and P were

incorporated by co-sputtering of B and  $P_2O_5$  targets in the SRO layers. It was found that high temperature *ex situ* furnace annealing at 1100 °C is required to form satisfactory Si NCs in the SRO layers for all samples doped and undoped. Therefore the structural, optical and electrical properties of only these thin films annealed at 1100 °C were further investigated. In summary GIXRD, HRTEM, EFTEM and PL results show that P doped films produced Si NCs with larger average size. On the contrary B doping seemed to only have a small effect on the average size of the Si NCs. HRTEM showed that the Si NCs in the B and P doped samples spanned the distance of many layers and the 1.8 nm SiO<sub>2</sub> layers were incapable of physically confining the Si NC growth. PL data confirms these results as P doped samples produced a strong red-shift in the spectrum which follows the quantum confinement effect. Electrical characterisation shows a large decrease in resistance in both types of doping compared to the intrinsic sample. Although there was a much larger decrease for the B compared to the P doping for the same target power that was used. Table 6.3 summaries and compares the main properties between the intrinsic, B and P doped SRO/SiO<sub>2</sub> bilayer samples.

	Intrinsic	Boron	Phosphorus
Average Si NC Diameter from GIXRD (nm)	9.1 ± 2.4	9.6 ± 2.0	11.1 ± 2.2
c-Si/a-Si ratio from Raman	0.65	0.68	0.73
PL peak position (eV)	1.32	1.32	1.48
Bulk resistivity from Hall ( $\Omega$ cm)	-	0.66	120

Table 6.3. Summary of the properties between intrinsic, B and P doped SRO/SiO<sub>2</sub> bilayers

Higher content Si in the SRO results in Si NC films with lower resistivity and higher absorption cross-sections. It is suggested that high Si content SRO is more useful in the current design of Si NC solar cell devices. The B doped SRO/SiO<sub>2</sub> material with its relatively low bulk resistivity of 0.66  $\Omega$ cm may actually allow a heterojunction type of photovoltaic structure with an *n*-type transparent conducting aluminium doped zinc oxide. This novel photovoltaic device structure made with high Si content SRO/SiO<sub>2</sub> bilayers is investigated in Chapter 8.

# Chapter Seven: Annealing Temperature and Treatment on the Properties of Aluminium Doped Zinc Oxide Thin Films<sup>††</sup>

## 7.1 Introduction

Si quantum dot (QD) solar cells require a high temperature annealing step in their fabrication as shown in the previous chapter. Mesa-structured Si QD solar cells fabricated at the University of New South Wales had issues with current crowding due to the high lateral resistance of the dielectric layers [209]. As a result, heavy current crowding occurs in the photovoltaic devices leading to loss in output current and voltage. Furthermore, the photovoltaic devices required precise plasma etching for metallization purposes as well as lithography that both increased the time and complexity of the fabrication process. A superstrate structure on transparent quartz substrates consisting of a front transparent conducting oxide (TCO) would be expected to improve carrier transport as a larger proportion of generated current would be flowing perpendicular to the junction in this type of structure. This concept is similar to thin-film amorphous-silicon (a-Si) or microcrystalline-silicon ( $\mu$ c-Si) and copper indium gallium (di)selenide (CIGS) solar cell designs.

Common TCOS such as indium and tin based oxides cannot withstand high annealing temperatures. However, ZnO has a very high melting point of 1975 °C, which makes it a prospective candidate material. Aluminium doped zinc oxide (AZO) has been successfully used in the past as a TCO for thin-film a-Si/µc-Si [152, 176, 178, 244] and CIGS [147, 245] solar cells. However, these solar cells do not require high temperature processes and therefore there has not been extensive investigation into the properties of AZO for high temperature processes. The purpose of this chapter is to investigate the properties of magnetron sputtered AZO thin films after high temperature annealing with different treatments. The main criteria that need to be investigated for good quality TCOs include:

<sup>&</sup>lt;sup>††</sup> See author's conference proceeding: T.C.-J. Yang *et al.,* "Investigation into High Temperature Post-Annealing of ZnO:AI as a Prospective Transparent Conductive Oxide Window Layer for Superstrate Silicon Nanostructure Solar Cells," in *29th European Photovoltaic Solar Energy Conference and Exhibition*, Amsterdam, The Netherlands, 2014, pp. 284 - 290.

optical transmission, conductivity and surface roughness. We demonstrate for the first time a method that allows annealing AZO films up to 1100 °C without completely decomposing the films and maintaining a low enough conductivity to makes the films attractive for their application in Si QD based solar cells.

## 7.2 Review of RF Magnetron Sputtered Aluminium Doped Zinc Oxide Thin Films

#### 7.2.1 Introduction

This section reviews the literature on radio frequency (RF) magnetron sputtered AZO thin films and examines the parameters of sputtering that produce the best quality films in order to create similar quality films for the work in this chapter. The general principles of magnetron sputtering are presented in the RF magnetron sputtering section of Chapter 4. Table 7.1 presents a comprehensive literature review survey of RF magnetron sputtered AZO thin films. The final column of Table 7.1 displays the list of authors and the year that their work was published in chronological order starting from Minami et al. [89] in 1984 to Hwang and Park in 2010 [246]. Column 1 of Table 7.1 lists the targets that were used in each experiment. Substrate heating (column 2) is also an important parameter as it helps with crystallisation of ZnO, activation of AI dopants and reducing surface roughness. The substrate temperature generally varies from room temperature (RT) to 300 °C. The 600 °C substrate temperature is a special case by Kim et al. [247] for epitaxial growth on sapphire (0001) substrates, but the resistivity of their film was much higher than the rest of the examples and was therefore not given in their journal publication. The pressure parameter (column 3) ranged from 0.5 - 30 mTorr from the various references. Usually a lower pressure allows for a slightly higher deposition rate due to the increased mean free path of the deposited species. The thickness (column 4) of the film is also an important parameter. Often, thicker films will result in large crystal grains and fewer grain boundaries per unit volume which means the mobility should be higher. Furthermore, the sheet resistance of the TCO will be lower as it is inversely proportional to the thickness. However an increase in thickness also means an increase in optical absorption of the film as well as higher material cost, hence there is always a trade-off between these factors when designing solar cells that use TCOs.

Target	T <sub>sub</sub> (°C)	Pressure	D (nm)	ρ (Ωcm)	N (cm <sup>-3</sup> )	ц	Comments	Ref. (year)
		(mTorr)				(cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )		
ZnO:Al <sub>2</sub> O <sub>3</sub> 2 wt.%	RT	Q	300	1.9 × 10 <sup>-4</sup>	$1.5 \times 10^{21}$	22	Substrate perpendicular to target	Minami <i>et al.</i> [89, 248] (1984-1985)
ZnO:Al <sub>2</sub> O <sub>3</sub> 2 wt.%	200	Q		3.3 × 10 <sup>-4</sup>	8.3 × 10 <sup>20</sup>	22.5	Substrate perpendicular to target	Minami <i>et al.</i> [249] (1989)
ZnO:Al <sub>2</sub> O <sub>3</sub> 2 wt.%	150	10	190	1.5 × 10 <sup>-4</sup>	1.3 × 10 <sup>21</sup>	32	Epitaxial film on sapphire (1210)	lgasaki & Saito [250] (1991)
ZnO:Al <sub>2</sub> O <sub>3</sub> 3 wt. %	150	7	150	4.7 × 10 <sup>-4</sup>	7.5 × 10 <sup>20</sup>	15		Park <i>et al.</i> [251] (1997)
ZnO:Al 2 wt. %	RT	Q	270	6.5 × 10 <sup>-4</sup>	$6.5 \times 10^{20}$	15		Cebulla <i>et al.</i> [252] (1998)
ZnO:Al 2 wt. %	270	0.5	1150 2	.8 × 10 <sup>-4</sup>	5.8 × 10 <sup>20</sup>	39		Kluth <i>et al.</i> [152] (1999)

Table 7.1. Literature survey of RF magnetron sputtered AZO films

ZnO:Al <sub>2</sub> O <sub>3</sub> 2 wt.%	600	10	1000		1.8 × 10 <sup>20</sup>	65.6	Epitaxial film on sapphire (0001) & post RTA at 900 °C in N <sub>2</sub>	Kim <i>et al.</i> [247] (2005)
ZnO:Al <sub>2</sub> O <sub>3</sub> 2 wt.%	250	1.5	1100	2.7 × 10 <sup>-4</sup>	3.2 × 10 <sup>20</sup>	ı	<i>N</i> est. from Burnstein-Moss effect	Song [253] (2005)
ZnO:Al <sub>2</sub> O <sub>3</sub> 2.5 wt.%	300	2	1153	1.9 × 10 <sup>4</sup>			<i>T<sub>sub</sub></i> dependence experiment	Yoo e <i>t al.</i> [244] (2005)
ZnO:Al <sub>2</sub> O <sub>3</sub> 5 wt.%	RT	30	430	3.0 × 10 <sup>-3</sup>	$4.1 \times 10^{21}$	0.5	Direct current magnetron sputtering	Li <i>et al.</i> [254] (2006)
ZnO:Al <sub>2</sub> O <sub>3</sub> 2 wt.%	200	15	500	T	8 × 10 <sup>20</sup>	24	Post H <sub>2</sub> treatment	Duenow <i>et</i> <i>al.</i> [147] (2008)
ZnO:Al₂O₃ 2 wt.%	100	25		1.2 × 10 <sup>-3</sup>	2.5 × 10 <sup>20</sup>	24.32	Further annealing in H <sub>2</sub> ; <i>ρ</i> improved to 5.63 × 10 <sup>-4</sup> Ωcm	Hwang & Park [246] (2010)

where,  $I_{sub}$  is the substrate temperature during the deposition in °C, d is the thickness of the AZO tilm.

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#### 7.2.2 Electrical Properties of Magnetron Sputtered AZO Thin Films

Columns 6, 7 and 8 list the resistivity  $\rho$ ; carrier concentration N; and Hall mobility  $\mu$  of the deposited ZnO:Al films respectively. Resistivity is one of the two most important parameters in TCOs. To obtain a low resistivity, the carrier concentration and mobility must be as high as possible. The lowest resistivity from the list (excluding epitaxial growth by Igasaki et al. [250] (1991)) is the first case by Minami et al. [89] in 1984. Over three decades ago, Minami et al. achieved a minimum resistivity of  $1.9 \times 10^{-4} \Omega$ cm with a mobility of 22 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and a high carrier concentration of  $1.5 \times 10^{21}$  cm<sup>-3</sup>. Minami *et al.* [89] found that the highest carrier concentration could be achieved with an  $AI_2O_3$  content of approximately 2% by weight with approximately 60% of the AI dopants electrically active. To act as a dopant and be active, the AI atoms in the films must be located on zinc lattice sites. To increase the percentage of active dopants, substrate heating or higher target powers are required. In addition, higher sputtering powers cause greater defects and damage to the film due to the higher intensity and deeper bombardment of sputtered species. Note, the sputtering power parameter has not been included in Table 7.1 as it is difficult to quantify and compare due to the large variability in the equipment configurations, e.g. target-to-substrate distances, etc for the different references. The optimum concentration of Al from Table 7.1 is approximately 2% by weight of Al<sub>2</sub>O<sub>3</sub>. A further increase in AI dopant content does increase the carrier concentration, however this increase is also accompanied by higher ionised impurity scattering resulting in a decrease in mobility. An example from Table 7.1 is the case by Li et al. [254] (2006), who uses a high Al<sub>2</sub>O<sub>3</sub> content of 5%, which yields a carrier concentration of  $4.1 \times 10^{21}$  cm<sup>-3</sup>, but only achieves a resistivity of 3.0 x  $10^{-3}$   $\Omega$ cm because the mobility is only 0.5 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. Furthermore, the transmittance at longer wavelengths drops owing to increased free carrier absorption. Bellingham et al. [255] investigates the fundamental physical limiting resistivity of TCO films and they theoretically calculated the limit of resistivity which they claimed to be about  $4 \times 10^{-5}$   $\Omega$ cm. This is about one order of magnitude lower than the resistivity values in Table 7.1.

#### 7.2.3 Structural Properties of Magnetron Sputtered AZO Thin Films

The structural properties that are most important to researchers in the area of AZO thin films are crystal orientation and grain size. Magnetron sputter-deposited ZnO crystallise easily; for most of the cases in Table 7.1 the predominant orientation is the (002) c-axis

orientation which is perpendicular to the substrate surfaces as it has the lowest surface free energy [256]. Song [253] investigated the effect of  $T_{sub}$ , working pressure and target power on the structural properties of radio frequency magnetron sputtering (RFMS) AZO films. He found that the sputtering rate increases with target power and decreasing working pressure. The average grain sizes that he obtained using the Scherrer equation for his different sputtering parameters were between 19–38 nm in diameter. He also concluded that higher substrate temperature (from RT up to 250 °C) resulted in larger grain size. The experimentally observed crystal microstructure of magnetron sputtered AZO can be explained well by Thornton's structure zone model [257, 258]. Song's experimental results together with other authors from Table 7.1 agree well with the model's general trend. The best quality AZO film deposition parameters appear to use  $T_{sub}$  between 200–300 °C, the lowest possible working pressure and a mid-range target power.

#### 7.2.4 Optical Transmittance Properties of Magnetron Sputtered AZO Thin Films

The transmittance versus wavelength graph is the most important optical characteristic of TCOs. A typical transmittance curve of AZO with different AI content is shown in Figure 7.1. Most magnetron sputtered AZO films have a relatively smooth surface without significant diffuse reflection; this is represented by the distinct interference fringes with deep valleys and high crests below 1000 nm. Most AZO on glass transmittance curves have an average transmission in the visible region (390-700 nm) of at least 80% and most have transmission 85% or higher. The AZO thin film itself actually has a higher transmission, but the glass or quartz substrate reflects/absorbs some of the incoming light. However, what is more important is how much the film absorbs, this can be calculated by Eq. 4.7 in Chapter 4, if the absolute transmission and reflection can be difficult to measure, however absorption can be directly measure through other techniques. Notice that one can tell if the film absorbs or not by observing the maxima in transmittance compared to the transmittance of the substrate (in this case glass or quartz).



**Figure 7.1.** Transmittance vs. wavelength of RFMS AZO ( $T_{sub} = 200 \text{ °C}$ ) films on Corning glass substrates with different Al content [147].

Another distinct characteristic of AZO film transmittance<sup>‡‡</sup> curves is the near the absorption edge of ZnO at 3.3 eV (380 nm). Here, as the AI content increases, i.e. increase in free carrier concentration, the absorption edge shifts monotonically towards higher energies (lower wavelengths). This phenomenon is called the Burnstein-Moss effect [259, 260]. From Figure 7.1, the absorption edge shifts from the ZnO (black) curve from approximately 380 nm progressively to the ZnO:AI 2 wt. % (green) curve at approximately 340 nm. Another distinct characteristic of doped ZnO films can be seen in the infrared region, the transmission starts to decrease for higher content AI doped samples. This is simply due to free carrier concentration, which causes the thin film to reflect in the near-infrared region. Duenow *et al.* [147] investigates the AI content of AZO films used in CIGS solar cells. They suggest that even though the optimum content is around 2 wt.% of AI, it may be better to use a lower content due to better transmission values at longer wavelengths which could provide higher current despite the slightly higher resistivity of the AZO.

#### 7.2.5 Summary

To achieve the lowest resistivity in AZO thin films, the mobility and free carrier concentration must be as high as possible. Higher mobility is achieved when films are

<sup>&</sup>lt;sup>‡‡</sup> N.B. Transmittance and (optical) transmission are essentially the same term and used interchangeably in this thesis.

single-axis orientated and consist of large grains. To achieve a high free carrier concentration, a high percentage of dopants must be active, as inactive dopants compromise the crystallinity. The literature for magnetron sputtered AZO thin films was extensively surveyed with the structural, electrical and optical properties briefly discussed. The magnetron sputtered AZO films have good TCO properties and appear promising for use with SRO/SiO<sub>2</sub> superlattice films to create Si QD solar cells. Using the information gathered from the literature review survey on RF magnetron sputtering, the next section outlines the experimental details including the parameters used to deposit the AZO thin films used in this chapter for annealing temperature dependence experiments.

### 7.3 Experimental Details

AZO samples were prepared by RF magnetron sputtering. The AZO thin films were deposited via a computer-controlled AJA ATC-2200 sputtering system with substrate heating set at 250 °C. Argon (Ar) was introduced into the sputtering chamber at 15 sccm with a pressure of 1.5 mTorr. Quartz substrates with high optical transmission over a large wavelength range and boron (B) doped *p*-type Si (100) wafers were used as the substrates. The substrates were cleaned in piranha solution (3:1 ratio of H<sub>2</sub>SO<sub>4</sub> to H<sub>2</sub>O<sub>2</sub>) for 15 minutes and then rinsed in deionised water prior to the deposition. The Si wafers were additionally dipped in 5% hydrofluoric acid (HF) for 30 seconds to remove the native oxide. The 4 inch target was ZnO:AI with 99.995% purity and 2.0 wt.% Al<sub>2</sub>O<sub>3</sub>. Sputtering was performed at two powers 150 W and 100 W with deposition rates of 2.17 nm/min and 1.91 nm/min respectively. The deposition rates were externally calibrated using variable angle spectroscopic ellipsometry (VASE), with a J.A. Woollam Co. M-2000 ellipsometer. The as-deposited thicknesses for the 150 W and 100 W samples were made to be approximately 250 nm, by adjusting the deposition time.

Three experiments were conducted:

 In the Preliminary Experiment (Section 7.4) ZnO and AZO samples were annealed at 1100 °C (to check that the films remained on the quartz substrate) followed by basic characterisation of their properties.

- 2) In Experiment 1 (Section 7.5), the 150 W samples were annealed at various temperatures ranging from 400-1100 °C for 1 hour in a 1 L quartz tube furnace with a N<sub>2</sub> flow rate of 2.5 L/min. The 150 W samples were also annealed at various temperatures ranging from 400-800 °C in a N<sub>2</sub> based forming gas (H<sub>2</sub> 4% / N<sub>2</sub> 96%) with the same flow rate.
- 3) In Experiment 2 (Section 7.6), the 100 W samples were annealed at 1100 °C for 1 hour in a 1 L quartz tube furnace with a N<sub>2</sub> flow rate of 2.5 L/min and allowed to cool to a lower temperature (below 150 °C) before removing from the furnace. Prior to the 1100 °C N<sub>2</sub> anneal, the quartz tube furnace was annealed together just with the quartz boat at 800 °C with Ar:H forming gas (see Section 7.6 for more details) to effectively 'clean' the furnace before the actual sample anneal.

The experimental tools and techniques used to characterise the material properties include: spectroscopic ellipsometry for thickness measurements, X-ray diffraction (XRD) for the crystallinity which includes the preferred crystal orientation and crystallite size, X-ray photoelectron spectroscopy for detection and estimation of the ratio of the constituent elements, four-point probe (4-PP) for sheet resistivity measurements, Hall effect measurements for the carrier concentration, mobility and resistivity, spectrophotometry for transmission, scanning electron microscopy (SEM) and atomic force microscopy (AFM) for surface morphology.

## 7.4 Preliminary Experiment

This preliminary experiment was conducted before the main experiments to assess their feasibility. For the preliminary experiment, intrinsic ZnO and AZO samples were prepared by RF magnetron sputtering. The sputtering powers to these targets were both 150 W. The rough thickness estimate was 330 nm. The same sputtering system was used for the deposition with substrate heating set at 250 °C. Argon and a small ratio of hydrogen gas (appoximately 1%) were introduced into the chamber at 15 sccm with a pressure of 1.5 mTorr. Only piranha cleaned quartz was used as substrates in this preliminary experiment. One sample of ZnO and one sample of AZO were annealed at 1100 °C in a 1 L quartz tube furnace for 1 hr with an Ar flow rate of 2 L/min.



**Figure 7.2.** Transmission of RF magnetron sputtered as-deposited and 1100 °C annealed ZnO and AZO films.

Figure 7.2 shows the transmission of the RF magnetron sputtered as-deposited and 1100°C annealed ZnO and AZO thin films as well as the transmission for a bare quartz substrate with no film deposition (control). The preliminary experiment showed that even after high temperature annealing at 1100 °C, the ZnO based films remained on the quartz substrates with high transmission in the visible spectral region (390-700 nm). For the ZnO, annealed ZnO and annealed AZO samples, there is a strong transition from absorption to transmission from 380 nm onwards and for the AZO samples from 345 nm onwards. These wavelengths coincide with the bandgap for ZnO at approximately 3.2 eV (388 nm). The doping of AI in the as-deposited AZO sample results in a slight blue-shift of the bandgap due to the Burnstein-Moss effect [259, 260]. The Burnstein-Moss effect occurs when the electron carrier concentration exceeds the conduction band-edge density of states, which usually happens with degenerately doped semiconductors. The extra electrons populate the conduction band which then pushes the Fermi level above the conduction band minimum causing an apparent shift in the bandgap as Pauli's exclusion principle does not allow excitation into these occupied states. In actual fact, the location of the Fermi level is not what causes the bandgap "widening" but rather the filling of states in the conduction band that causes the widening. The Burnstein-Moss bandgap widening

effect is related to the free electron carrier concentration,  $n_e$ , given by the following equation:

$$\Delta E_g = \frac{h^2}{8m_e^{*2}} \left(\frac{3}{\pi}\right)^{\frac{3}{2}} n_e^{\frac{2}{3}}$$
(7.1)

where, *h* is the Planck's constant and  $m_e^*$  is the effective electron mass in the conduction band. The opposite bandgap narrowing effects [261, 262] also compete with the Burnstein-Moss effect although their influence is usually much smaller here. This may be due to the relatively high activation energy for Al in ZnO which from different reports ranges from around 53 meV [263] to 65 meV [264].

The average optical transmission for all samples on quartz is greater than 83.1% in the visible range. For the as-deposited AZO sample, the transmission begins to drop significantly as the wavelength continues into the infrared region. This is caused by the signature free carrier absorption which is consistent for a low resistivity degenerately *n*-doped AZO sample.

	ZnO	AZO	Annealed	Annealed
			ZnO	AZO
Annealing Temperature (°C)	-	-	1100	1100
Annealing Time (hours)	-	-	1	1
Sheet Resistivity (k $\Omega$ / $\Box$ )	2700	0.050	>10,000	>10,000
Bulk Resistivity (Ωcm)	90	1.65 × 10 <sup>-3</sup>	>330	>330
RMS Surface Roughness	14.7	2.86	19.0	17.4

Table 7.2. Preliminary experiment parameters and results

Table 7.2 shows that the bulk resistivity of the intrinsic ZnO and AZO thin films are 90  $\Omega$ cm and 1.65 × 10<sup>-3</sup>  $\Omega$ cm respectively, however after annealing at 1100 °C in Ar, the electrical resistivity of both the thin films increases considerably. The reasons will be explained in the next section (Section 7.5).



**Figure 7.3.** AFM images of a) ZnO, b) AZO, c) annealed ZnO and d) 1100 °C annealed ZnO:AI thin films showing the surface roughness.

The root mean squared (RMS) surface roughness ( $\delta_{rms}$ ) of the films shown in Figure 7.3 are provided in Table 7.2. The AFM results show that after annealing, the ZnO RMS surface roughness increases from 14.7 nm to 19.0 nm and for the AZO sample from a low 2.86 nm to 17.4 nm. The low 2.86 nm RMS surface roughness for the as-deposited AZO, as seen

Figure 7.3b), is important for the purpose of this thesis, because additional SRO/SiO<sub>2</sub> bilayer thin films needed to be deposited on top to make up the active Si QD layers in Chapter 8. Additional texturing of AZO thin films through chemical or other means is an excellent way to provide light trapping properties. Textured AZO thin films are often used in amorphous Si [152, 176-178] and CIGS solar cells [265]. Unfortunately this thesis requires the deposition of thin bilayer films of SRO and SiO<sub>2</sub> down to a minimum thickness of 1.8 nm and because sputtering is a very directional deposition process, the surface

should ideally be as smooth as possible. Song in his PhD thesis (2005) has shown that in general, the lower the RF power to the sputtering target, the smaller the surface roughness [253].

## 7.5 Experiment 1

#### 7.5.1 Introduction

Minami *et al.* [89, 266] showed that the sheet resistance of magnetron sputtered ZnO thin films increase by "one to three orders of magnitude" when heat treated in vacuum and in inert gas ambients at 400 °C. This experiment is an extension of the studies by Minami *et al.* which involves post annealing 150 W sputter deposited thin film AZO samples at higher temperatures in N<sub>2</sub> and forming gas. Table 7.3 lists the different annealing temperatures and gases. For the first set (column 1) the samples were annealed up to 1100 °C in N<sub>2</sub> in a 1 L furnace. In the second set (column 2) the samples were only annealed up to 800 °C. This was due to the reduction reaction involving the H<sub>2</sub> and initially thought to be due to possible contamination with other materials in the "general purpose" large tube furnace. A second forming gas experiment was later conducted in a 1 L quartz tube furnace with similar results confirming the reduction by H<sub>2</sub> (no presented). In this experiment the samples were removed from the furnace at between 200-250 °C. The initial thickness of all the AZO thin films were 250 nm.

N <sub>2</sub> - 1 L furnace	Forming Gas – large
(°C)	tube furnace (°C)
400	400
600	500
800	600
1000	700
1100	800

Table 7.3. Annealing	temperature ar	ld gases
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#### 7.5.2 Optical Transmission Measurements



**Figure 7.4.** Transmission spectra of the AZO thin films annealed at different temperatures with  $N_2$  in a 1 L furnace.

Figure 7.4 shows the transmission spectra of the first set of samples annealed in N<sub>2</sub>. The as-deposited sample has an absorption edge at the lowest wavelength of 351 nm (at 50% transmittance) followed by the sample annealed at 400 °C at 365 nm and then 600 °C at 380 nm. There is no further change in the absorption edge from T4 to T6. This means that by annealing, there is a reverse in the Burnstein-Moss effect with loss in free carriers (electrons). In terms of free carrier absorption, the as-deposited sample has the highest absorption in the infrared region ( $\lambda$  = 700 nm), followed by the sample annealed at 400 °C. From 600 °C to 1000 °C, the transmission in the infrared region is almost identical. As for the sample annealed at 1100 °C, the transmission curve has changed significantly, indicating that the thickness, roughness and structure of the film has changed. Overall, it seems that post annealing AZO film causes the free carrier density to drop and Al no longer acts as a dopant (the reasons for this are given in Section 7.5.6).



**Figure 7.5.** Transmission spectra of the AZO thin films annealed at different temperatures with forming gas in a large tube furnace.

Figure 7.5, shows the transmission spectra of the samples annealed in forming gas at different temperatures. Again, there is a clear red-shift in the absorption edge (351 to 400 nm) for increasing post annealing temperatures from 400 to 500 °C. From 600 °C onwards however, the AZO films decompose completely from the reduction with  $H_2$  as their transmission spectra is similar to that of the quartz substrate (control) in Figure 7.2, where the transmission is high across the full wavelength range.

#### 7.5.3 Electrical Measurements

Table 7.4. Four-	-point probe	e resistivity	measurement results
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	Sheet Resistivity ( $\Omega/\Box$ )	Bulk Resistivity (Ωcm)
As-deposited	12.2	3.05 × 10 <sup>-4</sup>
400 °C (Nitrogen)	24.5	6.13 × 10 <sup>-4</sup>
400 °C (Forming Gas)	72.2	1.40 × 10 <sup>-3</sup>
600 °C (Nitrogen)	54,000	1.35 × 10 <sup>-1</sup>

	Mobility		Sheet	Bulk
	(cm²/Vs)	Carrier Density (cm <sup>-3</sup> )	Resistivity (Ω/□)	Resistivity (Ωcm)
As-deposited	21.0	1.16 x 10 <sup>-21</sup>	12.2	$2.56 \times 10^{-4}$
400 °C (N <sub>2</sub> )	14.2	4.67 × 10 <sup>-20</sup>	37.9	9.44 × 10 <sup>-4</sup>
400 °C (Forming Gas)	16.9	2.33 × 10 <sup>-20</sup>	72.2	1.58 × 10⁻³
600 °C (N <sub>2</sub> )	2.86	1.67 × 10 <sup>-19</sup>	62,400	2.15 × 10 <sup>-1</sup>

Table 7.5. Hall Effect measurement results

It is already well known that the increase in resistivity as a result of loss in carrier concentration is attributable to the "chemisorption" of oxygen into the ZnO films either from the surface or from oxygen trapped at defects such as grain boundaries [267, 268]. It is suggested that chemisorption of oxygen from the surface of films should be small if ambients such as high vacuum, inert gases and nitrogen are used [269]. Such chemisorption of oxygen in ZnO is important above 200 °C [266]. Table 7.4 shows 4-PP measurements of the AZO samples with various post annealing treatments. The samples that are not shown did not have low enough resistivity to produce a reading on the 4-PP system. Table 7.5 shows the Hall measurements of the same samples in Table 7.4. The values of the sheet and bulk resistivity of the films in both tables are consistent with one another. From the Hall Effect measurements, the lowest resistivity is the as-deposited sample with a bulk resistivity of 2.56  $\times$  10<sup>-4</sup>  $\Omega$ cm. After annealing in N<sub>2</sub> at 400 °C and 600 °C for 1 hour, the resistivity increases to 9.44  $\times$  10<sup>-4</sup>  $\Omega$ cm and 2.15  $\times$  10<sup>-1</sup>  $\Omega$ cm respectively. The resistivity continues to increase for post annealing temperatures after 600 °C. When the AZO film was annealed in forming gas at 400 °C for 1 hour, the resistivity increased to  $1.58 \times 10^{-3} \Omega$  cm which was slightly higher than the film annealed at 400 °C in N<sub>2</sub>. The higher increase in forming gas was surprising, because it was thought that hydrogen, being a shallow *n*-type dopant, would assist in the increase in free electron concentration. A few references have suggested that hydrogen acts as a shallow donor in ZnO [132, 133]. It also improves the conductivity of the AZO films if added to Ar in the sputtering process [147, 246]. Most interestingly Takata and Minami, et al. [270] showed that annealing in a hydrogen environment has the ability to rejuvenate the conductivity of AZO that was annealed up to 400 °C in air. The Hall measurements in Table 7.5 show that the carrier concentration is roughly two times higher in the sample annealed at 400 °C in  $N_2$  (4.67 × 10<sup>-20</sup> cm<sup>-3</sup>) than in forming gas (2.33 × 10<sup>-20</sup> cm<sup>-3</sup>). A possible explanation could be the deterioration of crystallinity with the reducing effect of forming gas. The carrier concentrations measured by the Hall Effect measurement system seems to correlate well with the optical transmission results in the previous section.



#### 7.5.4 Grazing Incidence X-ray Diffraction Measurements

**Figure 7.6.** GIXRD patterns of the AZO thin films annealed at different temperatures with  $N_2$  in a 1 L furnace.

The XRD patterns of the sample annealed in N<sub>2</sub> at different temperatures are shown in Figure 7.6. All samples displayed a strong peak around the  $2\theta^{\circ} = 34.5$  region, which signifies a strong (002) c-axis preferred orientation to the quartz substrate surface. This is due to the self-texturing phenomenon shown by Deng *et al.* [271]. The average grain size as calculated by the Scherrer equation was between 40 nm to 43 nm for all the samples, although there was no distinct pattern with the increased annealing temperature.



**Figure 7.7.** GIXRD patterns of the AZO thin films annealed at different temperatures with forming gas in a large tube furnace. Note, the 700 °C and 800 °C are not shown here as the film completely decomposes after this temperature.

Figure 7.7 shows the XRD patterns for the samples annealed in forming gas. The quartz substrate (control), with no film deposited is shown at the top of the figure. No peaks are visible for this quartz substrate control sample. For the 600 °C there are also no visible peaks, hence, the AZO thin film has completely decomposed and evaporated from the surface as a result of reduction from the H<sub>2</sub> in the forming gas. For the AZO thin film annealed at 400 °C the grain size actually increases from 43 nm (as-deposited) to 59 nm, however at 500 °C, the grain size decreases back down to 43 nm. At 500 °C the morphological change from reduction of the AZO film with the forming gas may have decreased the thickness and increased the surface roughness making the GIXRD intensity decrease resulting in a larger FWHM.

7.5.5 Atomic Force Microscopy and Scanning Electron Microscopy Analysis



Figure 7.8. SEM image of surface of the AZO sample annealed at 1000 °C in N<sub>2</sub>.

The SEM image of the AZO sample annealed at 1000 °C in N<sub>2</sub> (Figure 7.8) shows the typical surface morphology of the prepared RF magnetron sputtered AZO film. The grain size was measured by partitioning the y-axis into increments and then measuring the width of each of the grains along the x-axis. The average diameter of the grains from this analysis is  $77 \pm 5$  nm with a large standard deviation of 39 nm. The average grain size was also estimated by measuring each of the grains at its maximum width along the x-axis, which resulted in an upper estimated average diameter of 95 ± 5 nm with a standard deviation of 48 nm. The average grain size from this image is much larger than those determined by the Scherrer equation in the XRD analysis (40 - 43 nm), which actually give a lower estimate to the grain size. Note, however that the size of the grains in XRD is strongly affected by the size of the grain in the vertical direction (c-axis orientation), which may not be representative in the SEM image shown here. Also, in general, having a wide range of diameters would result in peak broadening determined by the smallest crystal grains. Ideally to produce the best quality film in terms of the lowest resistivity the larger the grains the better due to a decrease in grain boundary scattering.

 Table 7.6. RMS surface roughness of the 150 W RF magnetron sputtered AZO samples

 under various post annealing treatments

Treatment	<b>RMS Surface</b>
	Roughness (nm)
As-deposited	5.1
400 °C (N <sub>2</sub> )	6.6
400 °C (Forming Gas)	7.7
500 °C (Forming Gas)	11.5
600 °C (N <sub>2</sub> )	6.0
800 °C (N <sub>2</sub> )	8.6
1000 °C (N <sub>2</sub> )	17.4
1100 °C (N <sub>2</sub> )	49.0

Table 7.6 shows that there is a general increase in the RMS surface roughness with increasing annealing temperature. Annealing in forming gas also results in greater RMS surface roughness than in plain  $N_2$  up to a temperature of 500 °C. This would most likely be due to the some form of surface etching effect of the H<sub>2</sub> in the forming gas. From 1000 °C to 1100 °C, there is a significant increase in RMS surface roughness from 17.4 to 49.0 nm. This large change in surface roughness and possible subsequent coupling of light agrees well with the change in transmittance curves in Figure 7.4.

#### 7.5.6 X-ray Photoelectron Spectroscopy Analysis

XPS analysis of the AZO films was used to determine their elemental composition. A Thermo ESCALAB250Xi X-ray photoelectron spectrometer with a hemispherical energy analyser was used to carry out the measurements. The X-ray source was a monochromatic Al K $\alpha$  with energy of 1486.68 eV and the voltage, current and power to the X-ray source was 13 kV, 12 mA and 156 W respectively. A measurement area of approximately 0.3 mm<sup>2</sup> over the sample surface was used and the background pressure was 2 × 10<sup>-9</sup> mbar. The analysis was carried out by investigating the Zn 2p3, O1s A, O1s B, Al2p A, C1s A and Si2p core level spectra. The films were etched by means of Ar<sup>+</sup> bombardment at a rate of 5 Å/s for 240 s, which means that the measurements were taken

at a depth of approximately 120 nm from the surface of the thin films. The AZO thin films for the XPS analysis were deposited on the *p*-type Si wafer substrates.



**Figure 7.9.** Column graph of the atomic percentage of the major elemental species in the annealed AZO films as analysed by XPS.

Figure 7.9 shows the atomic percentage of the major elemental species in the sputter deposited AZO at different annealing temperatures in N<sub>2</sub> and at 400 °C in forming gas. For the samples annealed up to 1000 °C, the stoichiometry or the Zn-to-O ratio is in the range of 1:0.81-0.88. There is always an excess of Zn atoms which should in theory allow better conductivity if there are indeed interstitial Zn dopants, Zn<sub>i</sub> or oxygen vacancies, V<sub>o</sub> that should both contribute two free electrons as carriers each. Even though the sensitivity and precision of XPS is not as high as other elemental analysis instruments, an important result to gather from this analysis is that all the samples annealed up to 1000 °C still contain AI, which vary from 1.49-1.88 at.% and the as-deposited AZO thin film contains 1.67 at.% of AI. The AI does not evaporate exclusively from the film. When the as-deposited AZO film is thermally annealed, the resistivity rises as seen from the electrical measurements as well as the drop in free carriers as seen from the transmission measurements. Therefore, the majority of the AI atoms no longer acting as dopants. A possible explanation could be the diffusion and gettering/segregation of AI atoms from

active dopant sites to inactive regions such as grain boundaries or micro-pores as suggested in the past [249]. Clumping of AI atoms could also be a possibility. Another possibility is that increased temperature or increased oxygen partial pressures may cause oxidation of the AI in the film to the unwanted electrically inactive compound  $AI_2O_3$ . Thermodynamic arguments suggests that  $AI_2O_3$ , which has a free energy of formation,  $\Delta H_f$  of -1675.7 kJ/mol can be more easily formed than ZnO ( $\Delta H_f$  = -350.5 kJ/mol) [272]. Furthermore, the bond disassociation energies of AI-O and Zn-O is approximately 502 kJ/mol and 159 kJ/mol [272].

For the sample that was annealed at 1100 °C, which was the temperature at which the samples started to decompose, it seems that the film thickness has decreased. Evaporation of the surface layers of the AZO thin film may have occurred as well as a strong increase in surface roughness. The true final film thickness was not able to be estimated from ellipsometry and modelling of the dielectric constants as there was heavy inter-diffusion of Si from crystalline Si substrate and potentially Zn, O or Al into the wafer. If this was the case, the XPS results for the 1100 °C would have measured near the interface between the AZO film and the Si wafer substrate, which is very likely why the 1100 °C bar in Figure 7.9 produced higher atomic percentage readings of Si (3.0 at.%) and AI (10.0 at.%).

### 7.6 Experiment 2

#### 7.6.1 Introduction

Experiment 2 involves a special process that was discovered unintentionally. It was found that separately annealing the quartz tube furnace (with no samples inside) using Ar based forming gas consisting of 4% H<sub>2</sub> and 96% Ar prior to annealing the AZO samples at 1100 °C in N<sub>2</sub> causes the AZO thin film to partially retain its conductive nature. In addition, the furnace must be cooled down to at least 150 °C before removing the sample to prevent unwanted chemisorption of oxygen. Similarly, the N<sub>2</sub> flow rate during the annealing should be high. This discovery was made when reannealing post-annealed AZO films that lost their conductivity when annealed at 1100 °C in Ar based forming gas at 600 °C in hopes of rejuvenating the carrier concentration using hydrogen [270], unfortunately the AZO film also evaporated as in the previous experiments. Immediately after that Ar based forming

gas anneal, an 1100 °C N<sub>2</sub> anneal was done on as-deposited AZO films which unsuspectingly produced a 4-PP resistivity reading of approximately 2.2 k $\Omega/\Box$ .

The following experiment examines the 100 W sputter deposited thin film AZO samples which were annealed at 1100 °C in a 1 L quartz tube furnace with a flow rate of 2.5 L/min. Prior to the main 1100 °C N<sub>2</sub> anneal, the quartz tube furnace was pre-annealed together with the quartz boat at 800 °C using Ar based forming gas with a constant flow rate of 2.5 L/min. The ramping rate for the main 1100 °C N<sub>2</sub> anneal was 45 minutes from room temperature to 1100 °C; then the temperature was held at 1100 °C for 1 hour; finally the temperature was ramped down from 1100 °C to 150 °C in 120 minutes before the AZO samples were removed. Two separate experiments were conducted over separate weeks to ensure that this process was not a 'one-off' phenomenon. The separate experiments are labelled 'Run 1' and Run 2' in the following results.



#### 7.6.2 Optical Transmission Measurements

**Figure 7.10.** Transmission spectra of the 100 W AZO thin films annealed at different temperatures with  $N_2$  in a 1 L furnace with pre-forming gas treatment of the quartz tube.

Figure 7.10 shows the transmission spectra of the 100 W as-deposited AZO sample on quartz as well as two samples from the same deposition run that were annealed using the special 'pre-forming gas cleaning' technique described above. The as-deposited 100 W

sputtered AZO transmission spectra is similar to the 150 W sputtered AZO transmission spectra in Figure 7.4 apart from the fact that it has a slightly higher wavelength absorption edge as well as higher transmission in the infrared region, both due to its lower free carrier concentration. It has already been shown that a higher sputtering power provides more energy for the formation of the extrinsic AI dopants in the ZnO film resulting in higher free carrier concentration.

In Figure 7.10, the two samples from Run 1 and Run 2 both look very similar apart from the region below 370 nm where the AZO sample from Run 2 seems to have slightly higher transmission than the sample from Run 1. The difference in this spectral region below 370 nm in expected to be magnified because it is the strong absorbing region of ZnO hence any slight difference in properties such as the thickness or surface roughness or measurement random errors will show up here. Both samples from Run 1 and Run 2 show a red-shift in the absorption edge from 344 to 376 nm (at 50 % transmittance) compared to the as-deposited sample as well as an increase in transmission in the infrared region from approximately 1200 nm onwards. Again, both these phenomenon are attributed to the loss in free carrier concentration which would suggest that conductivity is lost completely, although from further electrical analysis discussed below, this was not the case.

#### 7.6.3 Ellipsometry Fitting Analysis

Spectroscopic ellipsometry (SE) is a useful although indirect technique that is used to analyse the optical properties of thin films. Variable angle spectroscopic ellipsometry (VASE) measurements were made using an M-2000VI VASE J.A. Woollam Co. Inc. ellipsometer on the thin film AZO samples. The wavelength range was measured from 381.4 to 1697.6 nm at incidence angles of 55°, 65° and 75°.

For the as-deposited AZO sample a pre-existing optical model consisting of a Drude oscillator, a Tauc-Lorentz (T-L) oscillator and a Gaussian oscillator was used to model the thin film. The Lorentz oscillator component is often used for amorphous semiconductors when coupled to an appropriate joint density of states near the bandedge and the Drude oscillator is often used for metals where there is high free carrier absorption.



**Figure 7.11.**  $\Psi$  values obtained by WVASE for as-deposited AZO on a Si wafer and its best fitting.



**Figure 7.12.**  $\Delta$  values obtained by WVASE for as-deposited AZO on a Si wafer and its best fitting.

The green lines from Figure 7.11 and Figure 7.12 show the respective  $\Psi$  and  $\Delta$  values obtained by WVASE for the 100 W sputter as-deposited AZO film on a silicon wafer measured with the ellipsometry beam at the centre of the wafer. The solid green lines from Figure 7.11 and Figure 7.12 show the best fit to the VASE data. From this particular ellipsometry measurement and fitting, the AZO film thickness was estimated to be 243.4 ±

0.2 nm. The mean squared error for the fitting was 17.8, which was slight higher than desired due to the poor fitting around the 400-500 nm region in Figure 7.11. Other points on the as-deposited AZO samples were also measured with an average thickness of approximately 245 nm.



Figure 7.13. Optical constants for the as-deposited AZO thin film.

Figure 7.13 displays the optical constants of the as-deposited AZO thin film. The optical constants are consistent with the AZO films measure previously by other authors and Kramers-Kronig consistent. The VASE measurements on the 1100 °C annealed AZO samples which were only deposited on quartz substrates were much harder to fit due to a few issues. Firstly the substrate was quartz which has a similar refractive index as the AZO thin film making the  $\Delta$  sensitivity much lower. Secondly, as seen from Table 7.6 after high temperature annealing at 1100 °C, the RMS surface roughness increases dramatically from 5.1 to 49.0 nm (see earlier sections). Even though the WVASE software allows modelling of surface roughness using an effective medium approximation layer (an averaged composition of certain percentage of film material and voids), the fitting is still very difficult. Hence the results for the modelling of the 1100 °C annealed AZO films are not shown here. However the modelling studies does suggest significant surface roughness (not presented).

#### 7.6.4 Electrical Measurements

The samples were measured using a Jandel RM3 system for 4-PP and an Ecopia HMS-5000 system in Van Der Pauw configuration for Hall measurements.

	$R_{sheet}$	R <sub>bulk</sub> (Ωcm)	Mobility,	Carrier
	<b>(Ω</b> /□)		μ	Concentration
			(cm²/Vs)	(cm <sup>-3</sup> )
As-deposited (4-PP)	22.0	5.50 × 10 <sup>-4</sup>	-	-
1100 °C (N <sub>2</sub> ) Run 1 (4-PP)	2,510	6.28 × 10 <sup>-2</sup>	-	-
1100 °C (N <sub>2</sub> ) Run 2 (4-PP)	3,020	7.56 × 10 <sup>-2</sup>	-	-
As-deposited (Hall)	21.5	5.15 × 10 <sup>-4</sup>	25.0	-4.85 × 10 <sup>20</sup>
1100 °C (N <sub>2</sub> ) Run 1 (Hall)	2,570	6.21 × 10 <sup>-2</sup>	12.7	-7.97 × 10 <sup>18</sup>
1100 °C (N <sub>2</sub> ) Run 2 (Hall)	3,280	6.96 × 10 <sup>-2</sup>	9.0	-1.02 × 10 <sup>19</sup>

Table 7.7. 4-PP and Hall measurements

Table 7.7 shows the 4-PP and Hall measurement results for the as-deposited 100 W AZO sample as well as the same AZO films annealed at 1100 °C in N<sub>2</sub> with a 'pre-forming gas cleaning' technique. Due to the difficulty in estimating the thickness of the 1100 °C annealed AZO films via VASE, the thickness was taken to be 250 nm in the conversion from the sheet to bulk resistivity calculation. From Table 7.7, the sheet resistivity and bulk resistivity for the 4-PP and Hall measurements are fairly similar. Looking at just the Hall measurements, the as-deposited sample has a sheet resistivity of 21.5  $\Omega/\Box$  and after the first and second anneal at 1100 °C, the sheet resistivity increases to 2,570 and 3,280  $\Omega/\Box$ respectively which is about an increase of two orders of magnitude in resistivity. The electron carrier concentration decreases from -4.85  $\times$  10<sup>20</sup> cm<sup>-3</sup> to -7.97  $\times$  10<sup>18</sup> cm<sup>-3</sup> and - $1.02 \times 10^{19}$  cm<sup>-3</sup>, which is still fairly high. This is still higher than even undoped ZnO films where the dominant carrier concentration comes from intrinsic defects, namely Zn interstitials,  $Zn_i$  and O vacancies,  $V_0$ . This could either mean that some of the extrinsic doped AI atoms (which remain in the film from the XPS measurements in Experiment 1) are still contributing to the carrier concentration and/or there has been an increase in the amount of intrinsic Zn<sub>i</sub> or V<sub>O</sub> defects as a result of the annealing process. The carrier mobility decreases by about 50% from 25.0 to 12.7 and 9.0 cm<sup>2</sup>/Vs which is unexpected, because given that there should be little change in the grain size from the GIXRD in

Experiment 1 there should be little change in the grain boundary scattering effect that is known to decrease mobility. The decrease in carrier concentration should actually assist in the carrier mobility due to a decrease in the ionised carrier scattering effect. Nevertheless, even after the high temperature 1100 °C anneals in N<sub>2</sub> the overall bulk resistivity from both runs (6.21 ×  $10^{-2} \Omega$ cm) and (6.96 ×  $10^{-2} \Omega$ cm) are below  $10^{-1} \Omega$ cm which is a typical range for ZnO. Subsequent annealing without the 'pre-forming gas' treatment resulted in samples with much higher sheet resistivities in the MΩ/□ region (not presented). Possible explanations for the retention of conductivity in this experiment include:

- The 'pre-forming gas' treatment removed any oxidising contaminants, perhaps residual oxides that may have caused unwanted chemisorption of oxygen from the surface of the AZO film.
- 2) Possible, but unlikely contamination from other species in the "general" anneal furnace.
- 3) Good isolation from the outside air and a high flow rate of N<sub>2</sub> at 2.5 L/min in a 1 L quartz tube furnace would have resulted in higher than atmospheric pressure inside the quartz tube which would have prevented or greatly reduced any admission of oxygen into the quartz tube during the anneal.
- 4) The removal of the sample at below 150 °C prevented oxidation of the film in air.
- 5) The AI impurities rather than the native defects are more stable donors against oxygen chemisorption [270] and may have still contributed to some extent to the free carrier concentration.

## 7.7 Conclusion

The preliminary experiment showed that both ZnO and AZO thin films deposited by RF magnetron sputtering can be annealed at 1100 °C without peeling, decomposing or evaporating. It was also shown that after high temperature annealing, these films retain high transmission properties and their surface roughness increases. Most importantly, both the resistivity of the ZnO and AZO thin films increases dramatically.

Experiment 1 showed that RF sputtered AZO films maintained their high optical transmission properties and high crystalline structure with a strong c-axis orientation after post-annealing even at temperatures up to 1100 °C. High c-axis orientation from XRD measurements in the past have been correlated to better conductivity due to larger grain sizes and conformal plains which aid in carrier transport. However, this experiment showed that resistivity begins to increase after annealing above a relatively low temperature of 400 °C. The main cause for the increase in resistivity is most likely the chemisorption of oxygen on the surface of the thin film or oxygen trapped at defects such as grain boundaries as suggested by various authors [266-268]. From XPS analysis, AI is still present in the thin films even after annealing 1100 °C, however most of the Al seems to be inactive and does not contribute significantly anymore to the free carrier concentration. One possible explanation is that there is diffusion and gettering of the AI into grain boundaries or internal micro-pores [249]. This leads to the assumption that perhaps a higher initial Al<sub>2</sub>O<sub>3</sub> content in the ZnO film could minimise the loss in resistivity after annealing at high temperature. Another possibility is microcracking of the thin films themselves due to thermal mismatch and stress, although this was ruled out due to the results in Experiment 2.

Experiment 2 showed that annealing the furnace with forming gas prior to annealing AZO samples actually allows the AZO samples to partially retain their conductivity. Removing the samples at a lower temperature (below 150 °C) from the furnace also reduces the loss in conductivity. The best 'pre-forming gas' furnace treatment 1100 °C annealed AZO thin films showed a sheet resistivity of around 2.5-3 k $\Omega/\Box$ . Although these values seem large for TCOs, compared to the intrinsic SRO/SiO<sub>2</sub> bilayers in the previous chapter (>1M $\Omega/\Box$ ), it is actually relatively small and can therefore are used for making prototype Si QD solar cell devices. The next chapter uses this 'pre-forming gas' furnace treatment technique in making *n-i-p* Si QD solar cells using transparent conducting AZO.

# Chapter Eight: Transparent Conducting Aluminium Doped Zinc Oxide for Superstrate Silicon QD Solar Cell Devices

## 8.1 Introduction

The previous chapter (Chapter 7) demonstrated how the transparent conducting oxide (TCO) aluminium doped zinc oxide (AZO) can partially retain its conductivity after annealing at 1100 °C in N<sub>2</sub> using a special "pre-forming gas anneal" method. Chapter 6 demonstrated the advantages of using high Si content in the SRO layers of the SRO/SiO<sub>2</sub> bilayer superlattice structure for fabricating Si nanocrystals (NCs). This chapter now combines the research work from both Chapter 6 and Chapter 7 to investigate a novel superstrate *n-i-p* Si QD solar cell device design. This new solar cell device is deposited on guartz substrates so the photovoltaic activity is only attributed to the Si NC layers compared to other designs that involve depositing the Si NC layers on conducting substrates such as crystalline Si (c-Si) wafers or poly-Si thin films. Furthermore, this Si QD solar cell device design is vertically structured meaning that it should avoid issues such as heavy current crowding and high series resistance as seen from previous mesa structured Si QD solar cell devices [209, 231]. The mesa devices also require precise plasma etching for metallisation purposes which increases the complexity during fabrication. This simple superstrate design on transparent quartz substrates consisting of a front transparent conducting AZO would be expected to improve carrier transport as a larger proportion of the generated current would flow perpendicular to the junction. Furthermore, larger device areas can be created with this design. This structure is similar to conventional thin-film solar cells which use TCOs [5]. A literature review survey of a few existing Si QD solar cell designs are given in the next section. In this chapter we demonstrate for the first time an attempt to fabricate a device using TCO and Si QDs. The device discussed here does not demonstrate a photovoltaic effect but the reasons for this are clearly identified. Potential disadvantages however of this new superstrate *n-i-p* Si QD solar cell device design include: 1) the cross-diffusion of elements between the AZO and the Si NC layers during the high temperature 1100 °C annealing step and 2) difficulty in reproducibility and low

yield due to this unwanted diffusion. Some ways to reduce these problems are discussed at the end of this chapter.

## 8.2 Review of Current Silicon QD Solar Cell Device Designs

As Si QDs are still in the research stages there have been few realisations of actual photovoltaic devices using this material. Most notably, the high temperature (1100 °C) annealing step needed to nucleate the Si QDs places severe requirements on the design of the devices. The issues include choice of substrate and separate contacts to the *n*- and *p*-type layers, thermal stability, thermal expansion coefficient mismatch, dopant diffusion and many more. For example, in almost all thin-film photovoltaics, a transparent conducting film - typically a transparent conducting oxide (TCO) - is needed for extraction of photocurrent; however most typical TCOs cannot withstand high temperatures and will decompose when exposed to temperatures as high as 1100 °C. In the case of the substrate glass, which is often used for thin-film solar cells, cannot be used for Si QD devices due to its lower melting point. Also, a lower annealing temperature for the solid phase nucleation of Si QDs is undesirable because passivation quality depends strongly on the thermal budget provided during the Si QD nucleation process [273]. This section reviews the recent developments in Si QD photovoltaic devices.
Photovoltaic Device Description	Substrate	Junction Type	Fabrication Method	V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA/cm²)	Ref.
(1) 25 boron/10 intrinsic/35 phosphorus doped SiO <sub>0.8</sub> (4 nm)/SiO <sub>2</sub> (2 nm) bilayers	quartz	n-i-q	RFMS	492	0.02	Perez-Wurfl <i>et</i> <i>al.</i> [209, 231] 2009, 2012
<ul> <li>(2) 30 bilayers of intrinsic <i>a</i>-Si<sub>1+x</sub>C:H (5 nm)/<i>a</i>-SiC:H (3 nm) sandwiched between <i>p</i>-type <i>a</i>-Si:H and <i>n</i><sup>++</sup>-type poly-Si</li> </ul>	quartz	d-i-u	PECVD	165	0.013	Kurokawa <i>et</i> <i>al.</i> [274, 275] 2008, 2010
<ul> <li>(3) 40 bilayers of intrinsic a-SiC<sub>1+x</sub>:O:H (5 nm)/<i>a</i>-SiC:O:H</li> <li>(2 nm) sandwiched between <i>p</i>-type <i>a</i>-Si:H and <i>n</i><sup>++</sup>-type poly-Si</li> </ul>	quartz	q-i-n	PECVD	518	0.34	Yamada <i>et al.</i> [276] 2010

Table 8.1. List of various Si QD photovoltaic devices from literature.

**{** 

(4) 30 bilayers of intrinsic a-	"membrane	n-i-p	PECVD	282	0.339	Löper <i>et al.</i>
Si <sub>1+x</sub> C:H (3 nm)/a-SiC:H (6	device"					[277-279]
nm) sandwiched between p-						2013, 2012,
type <i>a</i> -Si:C and <i>n</i> -type <i>a</i> -Si:C						2013
(5) 15 to 25 bilayers of	<i>p</i> -type Si	u-d	RFMS	556	29.8	Cho and Park
phosphorus doped SiO <sub>0.89</sub> (5	wafer					<i>et al.</i> [33, 280]
nm)/SiO <sub>2</sub> (2 nm)						2008, 2009
(6) 19 bilayers of boron doped	<i>n</i> -type Si	d-u	RFMS	463	19	Song <i>et al.</i>
a-Si <sub>1-x</sub> C <sub>x</sub> (6.5 nm)/SiC (2 nm)	wafer					[281, 282]
						2007, 2008
(7) 30 bilayers of phosphorus	<i>p</i> -type Si	u-d	RFMS	510	4.96	Di <i>et al.</i> [228]
doped SiO $_{0.3}$ (4 nm)/Si $_3N_4$ (2	wafer					2001
(mu						
(8) 250 nm of colloidal Si QDs	glass	Schottky	colloidal	510	0.148	Liu <i>et al.</i> [283]
with ITO and AI			synthesis			2010
where, RFMS and PECVD stan	nd for radio free	uencv magne	tron sputtering	and plasma	enhanced che	mical vapour

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deposition respectively.

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**Figure 8.1** Schematic diagram of an interdigitated Si QDs in SiO<sub>2</sub> superlattice mesas structure photovoltaic device [209].

Table 8.1 shows a list of various Si QD photovoltaic devices from literature to date. Although more than one device was produced for some of the references in the Table 8.1, only the champion device in terms of highest open-circuit voltage followed by short-circuit current density are shown. The list compiled is not meant to be a comprehensive list rather that the example devices were chosen to illustrate the advantages and disadvantages behind their device design. The first example in the list was implemented at the University of New South Wales by Perez-Wurfl et al. [209, 231] in 2009. The device consisted of multiple bilayers of SiO<sub>x</sub>/SiO<sub>2</sub> with co-doping through co-sputtering of B and P<sub>2</sub>O<sub>5</sub> to produce the p- and n-type regions respectively (shown in Figure 8.1). Reactive ion etching was used to create mesas to isolate the p-type from the n-type layers followed by evaporation of AI contacts. The main issue with this structure was the high resistivity of the bilayers which restricted the lateral current flow resulting in severe current crowding. In addition the bilayers were deposited on an insulating quartz substrate. The advance of this device structure is that the active regions that contribute to the photovoltaic effect entirely comprised of Si QD material as opposed to devices which were deposited on a c-Si wafer or poly-Si films. However, the main drawback with this device is its very low short-circuit current due to the heavy current crowding and high series resistance.



**Figure 8.2.** Schematic diagram of Si QDs in SiC superlattice photovoltaic device structure [274].

The second photovoltaic device in the list was fabricated by a research group in Japan [274] who designed Si QDs in SiC matrices between *p*-type *a*-Si:H and  $n^{++}$ -type poly-Si on quartz. The third photovoltaic device was fabricated by the same authors who improved on the structure by the addition of oxygen in the intrinsic Si QD/SiC layers and the reduction in the sheet resistance of the  $n^{++}$ -type layers [276]. The first drawback from this device structure is the potential diffusion of dopants or even Si from the *p*-type *a*-Si:H and especially the heavily doped  $n^{++}$ -type into the intrinsic Si QD/SiC bilayers and the subsequent effect it has on crystallisation and characteristics of the Si QD/SiC bilayers. In addition, it is difficult to separate the photovoltaic effect of the Si QD/SiC material from that of the rather thick high quality poly-Si layer. For these reasons the open-circuit voltage (518 mV) and short-circuit current density (0.34 mA/cm<sup>2</sup>) are higher than those of the first photovoltaic device by Perez-Wurfl *et al.* 



**Figure 8.3.** Schematic diagram of the Si QD in SiC photovoltaic membrane device. The grey areas represent insulation layers separating the active regions from the c-Si wafer [277].

The "membrane device" presented by Löper et al. [277, 278] allows selective characterization of the Si QDs in SiC matrix material. The basic fabrication steps of this device, shown in Figure 8.3, starts with the deposition of multiple Si<sub>1+x</sub>C:H/SiC:H bilayers with buffer layers on either side on oxidised c-Si wafer substrates followed by a high temperature thermal anneal (>1000 °C) in N<sub>2</sub> to nucleate the Si QDs. An *n*-type *a*-Si<sub>x</sub>C<sub>1-x</sub>:H layer is then deposited on the bottom side. Inkjet resist masking allowed isolation of desired regions for local chemical etching through the c-Si wafer down to the Si QD/SiC bilayers. A p-type a-Si<sub>x</sub>C<sub>1-x</sub> layer is then deposited followed by ITO on the top and bottom of the device. This device fabrication bypasses the need for *in situ* doping of the *n*- and *p*type layers so no diffusion of dopants occurs during the process. No high temperature processes are needed other than for the Si QD/SiC superlattices, which means full flexibility in the choice of materials for the selective contacts, e.g. ITO in this case. The main disadvantages of this device structure are its complexity and fabrication time. There are many steps involved in the fabrication of this device structure which means it would never be commercially viable. In terms of performance, as charge carrier mobility and lifetime are much higher in the Si wafer than in the Si QD/SiC superlattice layers, the two materials have to be separated very carefully from each other with no pinholes or unintentional etching into the insulation layers as shown from SEM images in Ref. [278].

Furthermore, only small area devices can be fabricated due to the mechanical integrity of the thin "Si QD/SiC membrane" during the etching.



**Figure 8.4.** Schematic diagram of a heterojunction photovoltaic device consisting of an *n*-type Si QD/SiO<sub>2</sub> bilayered superlattice on a *p*-type Si wafer with Al contacts (not to scale) [280].

The fifth to seventh Si QD photovoltaic devices in Table 8.1 all consist of Si QD superlattices deposited on c-Si wafers, an example is shown in Figure 8.4. These devices have much higher short-circuit current densities than all the other devices in Table 8.1 simply because the Si wafers (with superior electronic properties) are contributing mostly to the photocurrent rather than the Si QD/Si dielectric superlattice layers. Furthermore the Si wafers (in the thickness range of 100-500 µm) are much thicker than the thin film Si QD/Si dielectric superlattices (<1 µm) which allows much more absorption of the incoming light. Furthermore, the high temperature anneal to create Si QDs would result in an unwanted diffusion of dopants into the Si wafer creating an active junction on the wafer and further explaining the relatively high short circuit current and open circuit voltage of these devices. The advantages of this device structure are its simplicity, short fabrication time and good consistent repeatability. The ability to produce large area devices is also a benefit. Thin films of Si rich dielectric/Si dielectric bilayered superlattices are simply deposited directly onto c-Si wafers and annealed at high temperature to form the Si QDs. A major drawback could be the cross-dopant contamination at the interface. Another major downside is the difficulty in separating the photovoltaic effect between the two materials, even though this structure is intended to be a heterojunction structure. Initially, this device

might seem quite impractical in assessing the properties of the Si QD/Si dielectric superlattice material, because the majority of the photovoltaic contribution seems to occur in the c-Si wafer, but because the fabrication is very quick and simple, many devices can be made. Therefore comparison with slight variations in a particular parameter of the Si QD/Si dielectric bilayers, such as thickness, Si richness and number of layers can be characterised quickly and in large quantities. Furthermore, ultimately the goal of third generation Si QD photovoltaics is to produce an "all-Si" tandem cell with a c-Si wafer as the bottom sub-cell.

Figure has been removed due to Copyright restrictions Refer to Fig. 1 in C. Y. Liu and U. R. Kortshagen, "A Silicon Nanocrystal Schottky Junction Solar Cell produced from Colloidal Silicon Nanocrystals," Nanoscale Res Lett, vol. 5, pp. 1253-6, 2010.

Figure 8.5. Schematic diagram of a colloidal Si QD Schottky photovoltaic device [283].

This final device is quite interesting because it is the only device in the list that does not require high temperature annealing to form the Si QDs, which comes as an advantage for device design. The Si QDs or NCs were synthesized by a "non-thermal plasma reactor under vacuum" [283], through the dissociation of silane precursor (SiH<sub>4</sub>). For more information on the colloidal synthesis of the Si QDs, refer to Refs. [283, 284]. The Si QDs were then spin-coated multiple times onto ITO on glass substrates with Al contacts deposited onto the other side. The authors mention that traditionally, the synthesis of colloidal Si NCs involves passivation by co-ordinating ligands that also provide solubility. However they managed create these Si NCs without the involvement of ligands. This in turn reduces the fabrication steps, cost and allows better large scale manufacturability of this type of Si QD photovoltaic device.

# 8.3 Experimental Details

# 8.3.1 Introduction

The following experimental details are separated into two sections:

- 1) The first section (Section 8.3.2 AZO Superstrate *n-i-p* Solar Cell Devices on Quartz) outlines the fabrication details for the AZO superstrate *n-i-p* solar cell devices. These devices were fabricated by first depositing AZO and then sputtering high Si content SRO/SiO<sub>2</sub> bilayers through a metallic mask with an *n-i-p* configuration. Then the samples were annealed at 1100 °C using the special "preforming gas clean" annealing technique outlined in Chapter 7 to allow the AZO to partially retain its conductivity.
- 2) The second section (Section 8.3.3 Superstrate AZO on B and P bilayers) outlines the fabrication details for the AZO on boron (B) or phosphorus (P) devices which were fabricated to investigate the interface properties between the **as-deposited AZO** and annealed B or P high Si content SRO/SiO<sub>2</sub> bilayers. The B or P bilayers were annealed at 1100 °C first and then the AZO was deposited.

The important difference between the first and second devices is that in the second device the AZO did not undergo any annealing. After fabrication, the devices were characterised using a four-point probe (4-PP) system, quasi-steady-state  $Suns-V_{oc}$  system and Darkstar *I-V* system. An elemental depth profile was also obtained by ToF-SIMS for one of the AZO superstrate *n-i-p* solar cell devices. Characterisation was done before and after Al metallisation.





**Figure 8.6.** Schematic diagram of the final superstrate *n-i-p* Si QD solar cell device structure.

Figure 8.6 shows the cross-sectional schematic illustration of the final superstrate n-i-p Si QD solar cell device. The vertical design structure should ideally reduce the series resistance and current crowding. The steps for fabricating this novel superstrate n-i-p Si QD solar cell device structure is shown below:

- Quartz substrates with high optical transmission over a large wavelength range and high melting point (>1600 °C) were used as substrates. These quartz substrates were cleaned in piranha solution (3:1 ratio of 96% concentrated H<sub>2</sub>SO<sub>4</sub> to 30% H<sub>2</sub>O<sub>2</sub> solution) for 15 minutes then rinsed in deionised water and dried with N<sub>2</sub> before placing them in the load-lock chamber of the sputtering system.
- 2) AZO thin films were deposited via a computer-controlled AJA ATC-2200 sputtering system with substrate heating set at 250 °C. Argon (Ar) was introduced into the sputtering chamber at 15 sccm with a pressure of 1.5 mTorr. The 4 inch target was ZnO:Al with 99.995% purity and 2.0 wt.% Al<sub>2</sub>O<sub>3</sub>. Sputtering was performed at 100 W with a deposition rate of 1.91 nm/min. The deposition rates were externally calibrated using variable angle spectroscopic ellipsometry (VASE), with a J.A. Woollam Co. M-2000 ellipsometer. The as-deposited thicknesses for the samples

were 250 nm. This was achieved by adjusting the deposition time. The deposition method is similar to the work discussed in Chapter 7.

- 3) A metallic mask (shown in Figure 8.7) with square openings (8 mm x 8 mm) was then placed between the quartz and the incoming sputtered particles. Bilayers of SRO/SiO<sub>2</sub> were deposited in the same magnetron sputtering system at room temperature. Radio frequency (RF) power supplies (13.56 MHz) were connected to a 4 inch intrinsic Si and 4 inch SiO<sub>2</sub> target. Boron (B) and phosphorus (P) doping was achieved via co-sputtering with either a 2 inch B or 2 inch P<sub>2</sub>O<sub>5</sub> target. Argon was injected into the chamber at a rate of 15 sccm with the chamber pressure maintained at 1.5 mTorr. The RF power to the Si and the SiO<sub>2</sub> targets were 203 W and 90 W respectively with a combined deposition rate of 3.46 nm/min. The SiO<sub>2</sub> rate at 90 W was 1.04 nm/min. The resultant volume ratio of Si:SiO<sub>2</sub> was approximately 7:3. The deposition rates were calculated ex situ via spectroscopic ellipsometry. According to the estimated sputtered target densities of the Si and SiO<sub>2</sub> thin films, the calculated stoichiometry is approximately SiO<sub>0.3</sub>. The bilayers were made to be 4 nm thick SRO and 1.8 nm of SiO<sub>2</sub> respectively. B and  $P_2O_5$ targets were co-sputtered in the SRO layers with a target power of 25 W each. 20 B doped bilayers were deposited followed by 40 intrinsic (undoped) bilayers and then 20 P<sub>2</sub>O<sub>5</sub> doped bilayers. A final 20 nm SiO<sub>2</sub> capping layer was deposited to protect the film from oxidation and contamination during standby and annealing stages. The deposition method is similar to the work discussed in Chapter 6.
- 4) The samples were then annealed at 1100 °C for 1 hour in a 1 L quartz tube furnace with a N<sub>2</sub> flow rate of 2.5 L/min and allowed to cool to a lower temperature (below 150 °C) before removing from the furnace. Prior to the 1100 °C N<sub>2</sub> anneal, the quartz tube furnace was annealed along with the quartz boat at 800 °C with Ar based forming gas. See Chapter 7 for more details.
- 5) The next step involved the removal of the 20 nm SiO<sub>2</sub> cap. Two methods were employed:
  - By isolating the AZO and *n-i-p* Si QD regions with special vacuum tape and then dipping in 5% HF solution for 30 s. Only 30 s was used as opposed to

the usual 90 s because in some instances the HF solution removed some of the underlying AZO thin film which completely undercut the *n-i-p* regions.

- By photolithography. The steps were: spinning positive AZ6632 photoresist at a speed of 4000 rpm for 30s; prebaking at 95 C for 5 min; exposing for 10 s using a Quintel 6000 mask aligner equipped with an UV light source (365 nm) with a measured intensity of 10 mW/cm<sup>2</sup> (no postbaking); submerging in AZ326MIF developer for 60 s to fully remove the exposed photoresist. Dipping in HF for 90 s and rinsing in deionised water. Finally dipping in acetone for 30 s to remove the remaining photoresist and rinsing again in deionised water.
- 6) Finally metal contacts were deposited onto the *n-i-p* Si QD and AZO regions. Al was chosen for the metal contacts as Al has a low specific contact resistance to ZnO which is in the range of  $\approx 10^{-5} \Omega \text{cm}^2$  [285, 286]. This low specific resistivity is due to the formation of an Al to ZnO interfacial phase which occurs at room temperature [286]. The high doping density of the *n*-type Si QD layers would also ensure an ohmic contact. Approximately 500 nm of Al was evaporated onto the *n-i-p* Si QD and AZO regions using an INTERCOVAMEX H2 thermal evaporator. The final schematic superstrate *n-i-p* Si QD solar cell device structure is shown in Figure 8.6.



**Figure 8.7.** Image of the metallic mask used in the sputtering of the *n-i-p* regions of the superstrate Si QD solar cell device.



**Figure 8.8.** Photographs of the final AZO superstrate *n-i-p* Si QD solar cell device structure before (a) and after (b) AI metallisation.

## 8.3.3 Superstrate AZO on B and P bilayers



**Figure 8.9.** Schematic diagram of the final superstrate AZOonB and AZOonP device structure.

- Quartz substrates were cleaned in piranha solution for 15 minutes then rinsed in deionised water and dried with N<sub>2</sub> before placing them in the load-lock chamber of the sputtering system.
- 2) 20 bilayers of either B or P<sub>2</sub>O<sub>5</sub> doped SRO/SiO<sub>2</sub> were deposited by magnetron sputtering at room temperature. RF supplies were connected to a 4 inch intrinsic Si and 4 inch SiO<sub>2</sub> target. Doping was achieved via co-sputtering with either a 2 inch B or 2 inch P<sub>2</sub>O<sub>5</sub> target. Argon was injected into the chamber at a rate of 15 sccm with the chamber pressure maintained at 1.5 mTorr. The RF power to the Si and the SiO<sub>2</sub> targets were 203 W and 90 W respectively with a combined deposition rate of 3.46 nm/min. The SiO<sub>2</sub> rate at 90 W was 1.04 nm/min. The resultant volume ratio of Si:SiO<sub>2</sub> was approximately 7:3. The deposition rates were calculated *ex situ* via spectroscopic ellipsometry. According to the estimated sputtered target densities of the Si and SiO<sub>2</sub> thin films, the calculated stoichiometry is approximately SiO<sub>0.3</sub>. The bilayers were made to be 4 nm thick SRO and 1.8 nm of SiO<sub>2</sub> respectively. B and P<sub>2</sub>O<sub>5</sub> targets were co-sputtered in the SRO layers with a target power of 25 W each. A final 20 nm SiO<sub>2</sub> capping layer was deposited to protect the film from oxidation and contamination during standby and annealing stages. The method is similar to the work discussed in Chapter 6.
- 3) The samples were then annealed at 1100 °C for 1 hour in a 1 L clean quartz tube furnace with a N<sub>2</sub> flow rate of 2.5 L/min and allowed to cool to a lower temperature (below 150 °C) before removing from the furnace.
- 4) The SiO<sub>2</sub> caps on both the B and P doped SRO/SiO<sub>2</sub> bilayer samples were removed by dipping in 5% HF solution for 90 seconds.
- 5) The samples were rinsed in deionised water and dried before placing them in the load-lock chamber of the sputtering system. A metallic mask (shown in Figure 8.7 on the next page) with square openings (8 mm x8 mm) was placed between the quartz and the incoming sputtered particles.
- 6) AZO thin films were deposited with substrate heating set at 250 °C. Argon (Ar) was introduced into the sputtering chamber at 15 sccm with a pressure of 1.5 mTorr.

The 4 inch target was ZnO:Al with 99.995% purity and 2.0 wt.%  $Al_2O_3$ . Sputtering was performed at 100 W with a deposition rate of approximately 1.57 nm/min. The deposition rates were externally calibrated using variable angle spectroscopic ellipsometry (VASE), with a J.A. Woollam Co. M-2000 ellipsometer. The as-deposited thicknesses for the samples were 410 nm. This was achieved by adjusting the deposition time. The method is similar to the work discussed in Chapter 7.

7) Finally AI metal contacts were deposited. Approximately 500 nm of AI was evaporated onto both the B and P doped and AZO regions. The final schematic AZOonB and AZOonP device structure is shown in Figure 8.9 and photographs of the final AZOonB and AZOonP devices before and after AI metallisation are shown in Figure 8.10(a) and (b) respectively.



**Figure 8.10.** Photographs of the final AZO on B (left) and P (right) 20 high Si content  $SRO/SiO_2$  bilayer devices before (a) and after (b) AI metallisation.

# 8.4 Results and Discussion

### 8.4.1 Time-of-Flight Secondary Ion Mass Spectroscopy Analysis



**Figure 8.11.** Optical microscopy image of the sputter and analysis area after the ToF-SIMS depth profile measurement of the AZO superstrate *n-i-p* solar cell device before AI metallisation (top left), elemental maps of the analysis area (bottom) and the elemental maps side by side to the analysis area (top right).

In order to study the cross-diffusion of the different elemental species, ToF-SIMS was employed to obtain a depth profile of one of the AZO superstrate *n-i-p* solar cell devices before AI metallisation. An IONTOF GmbH TOF.SIMS5 system was used for the depth profile measurement and  $O_2^+$  was used as the sputtering source in positive polarity to enhance the detection of the positive ions (B<sup>+</sup>, AI<sup>+</sup>, Si<sup>+</sup>, P<sup>+</sup> and Zn<sup>+</sup>). This however meant that the oxygen could not be one of the elements detected. Figure 8.11 shows an optical microscopy image of the analysis and sputter area after the ToF-SIMS depth profile measurement. The sputter area was 300 × 300  $\mu$ m<sup>2</sup> and the actual analysis area was 99.6  $\times$  99.6  $\mu$ m<sup>2</sup>. The optical image shows an inhomogeneous surface with dark spots which coincide with the profile of the AI<sup>+</sup> and Si<sup>+</sup> elemental maps.





Figure 8.12 shows the ToF-SIMS depth profile of the superstrate AZO *n-i-p* solar cell device. The total sputtering time, *t*, was 2500 s over a total thickness of approximately 941 nm with an average sputter rate of 0.38 nm/s. Note that the intensities are only relative values (a.u.) as there were no standard samples for referencing. However this analysis was sufficient for the purpose of this experiment. From the depth profile the first 270 s of sputtering time corresponds to the first 20 P doped SRO/SiO<sub>2</sub> bilayers, this is around the region where the P<sup>+</sup> concentration begins to drop off sharply (blue curve shoulder). The region between 270 s to approximately 810 s corresponds to the intrinsic SRO/SiO<sub>2</sub> bilayers. From 810s to approximately 1080 s is the B doped regions, although the region (red curve) does not seem as well defined as the P side due to the higher B diffusion rates in Si and SiO<sub>2</sub>. The B<sup>+</sup> and P<sup>+</sup> curves seem to make a fairly uniform *n-i-p* junction given that their depth profile is similar to the ToF-SIMS results from Perez-Wurfl *et al.*'s Si NC *p-i-n* diodes [209]. From a sputtering time of 1100 s to approximately 1720 s is the AZO layer and the remaining is the quartz substrate.

From the depth profile, the first noticeable issue with this AZO superstrate *n-i-p* device is the significant diffusion of AI and Zn from the surface shown by the grey and green curves respectively. This would most likely cause heavy unwanted shunting to the devices. The concentration of AI diffusing from the surface is  $6 \times 10^4$  a.u. at t = 0 s and the concentration of AI from the AZO layer is approximately  $8 \times 10^5$  a.u. at t = 1400 s, which is only just over an order of magnitude larger. If we assume that the initial AZO layer with 2% by weight Al<sub>2</sub>O<sub>3</sub> has around 1.3  $\times$  10<sup>21</sup> Al atoms/cm<sup>-3</sup> then (i.e. 8  $\times$  10<sup>5</sup> a.u.), then the concentration of AI diffusing from the surface on the P region would be around  $9.8 \times 10^{19}$ atoms/cm<sup>-3</sup>. This is actually a significant amount and in the same order of magnitude if we compare it to the concentration of the B and P which from similar experiments in the past involving B and P doping of SRO/SiO<sub>2</sub> with similar sputter target powers in the range of 5  $\times$  $10^{19}$  to 6 x  $10^{20}$  atoms/cm<sup>-3</sup> [70, 71, 209]. Given the localisation of the Al into spots on the surface, as seen from the elemental map in Figure 8.11, the actual shunting effect would be even more severe than what the concentration alone suggests. Similarly there is Zn diffusion from the surface with a concentration of  $2 \times 10^3$  a.u. at t = 0 s, although this is around 2 orders of magnitude less when compared to the concentration of the Zn in the AZO region at approximately  $1.5 \times 10^5$  a.u. at t = 1400 s. From the interface between the B SRO/SiO<sub>2</sub> bilayers and the AZO there is also heavy cross-diffusion of dopants. Both the Zn and especially the AI (given its smaller ionic radius) diffuse into the SRO/SiO<sub>2</sub> and the B and Si into the AZO. The cross-diffusion was much worse than originally expected.

### 8.4.2 Four-Point Probe Measurements

4-PP measurements were performed on all the samples before AI metallisation:

- 1) The AZO region of the AZO superstrate *n-i-p* Si QD solar cell device (tape) had a higher sheet resistance between 100-200 k $\Omega/\Box$  which was higher than expected (see Chapter 7). The top of the *n* layer had a sheet resistance between 150-400 k $\Omega/\Box$ .
- 2) For the AZO region of the AZO superstrate *n-i-p* Si QD solar cell device (lithography) which was annealed in a separate run from the previous device had an even higher sheet resistance between 1-2 M $\Omega$ / $\Box$ . The top of the *n* layer had a sheet resistance between 150-200 k $\Omega$ / $\Box$ . The unexpected high resistance for this device and the previous one is again probably due to the heavy cross-diffusion of elements which seems to have degraded the desired properties of both the *n-i-p* and AZO regions.
- 3) For the AZOonB sample, the sheet resistance of the B layers was 45 k $\Omega/\Box$ . The AZO layer on top of the B layers was 20.0  $\Omega/\Box$ .
- 4) For the AZOonP sample, the sheet resistance of the P layers was 1.0-1.4 MΩ/□. The AZO layer on top of the P layers was 19.0 Ω/□. However, the same AZO deposition on insulating quartz (control) had a lower sheet resistance of 11.2 Ω/□. The difference between the AZO and the AZO on B and P could be a result of small cross-diffusion of elements across the interface during the AZO deposition which required substrate heating at 250 °C.

### 8.4.3 I-V Measurements

Dark and light *I-V* curves were measured using an in-house built DarkStar *I-V* tester. All the dark *I-V* measurements were measured with the quartz substrate facing down on the temperature stage which was set to 25 °C. The light *I-V* was measured with the substrate

facing up on a transparent glass stage which meant that the temperature could not be controlled. The halogen lamp had a spectrum close to AM 1.5.



**Figure 8.13.** *I-V* curves of the AZO superstrate *n-i-p* solar cell devices in the dark before and after AI metallisation and with illumination (light). HF dip using (a) tape and (b) photolithography.

Figure 8.13 shows the *I-V* curves of the AZO superstrate *n-i-p* solar cell devices in the dark before and after AI metallisation and with illumination (light). Figure 8.13(a) shows the *I-V* curves for the sample which was etched for 30 s in HF to remove with 20 nm SiO<sub>2</sub> capping using tape to isolate the regions, whereas Figure 8.13(b) shows the *I-V* curves for the sample which was etched for 90 s in HF using photolithography to isolate the regions. From both figures (a) and (b) it can be seen that the AZO superstrate *n-i-p* solar cell devices do not produce rectifying junction responses (diode like *I-V* curves) and are hence not strictly solar cells. The heavy cross-contamination and mixing of AI and Zn across the *n-i-p* region as seen from the ToF-SIMS results seemed to have caused heavy shunting of the devices. From Figure 8.13(a) the graph shows a linear *I-V* response near the origin (0.00 V, 0.00 A) for all three curves which show a typical resistor type of device as a result of the heavy AI shunting. The curve starts deviating from the ideal linear response at higher voltages, but this could be due to a number of reasons such as high carrier injection or high field effects for which the exact nature cannot be deduced from *I-V* measurements alone. The resistance however can be estimated by the inverse of the gradients near the

origin which were 7.1 × 10<sup>5</sup>, 7.1 × 10<sup>5</sup> and 3.1 × 10<sup>5</sup>  $\Omega$  (V/A) for the dark *I-V* before and after AI metallisation and light *I-V* after AI metallisation respectively. Similarly the *I-V* curves (Figure 8.14(b)) of the photolithography device show a linear *I-V* response near the origin. The resistance as estimated by the inverse of the gradients near the origin were 9.6 × 10<sup>3</sup>, 3.4 × 10<sup>3</sup> and 3.8 × 10<sup>3</sup>  $\Omega$  (V/A) for the dark *I-V* before and after AI metallisation and light *I-V* after AI metallisation respectively. The initial resistance of the sample with the SiO<sub>2</sub> cap removed using photolithography is lower than the sample using tape. However the conductivity improves much further once the AI is applied to the photolithography sample than the tape sample due to the higher initial sheet resistance of the AZO in the photolithography sample.



**Figure 8.14.** *I-V* curves of the AZO on (a) B and (b) P devices in the dark before and after AI metallisation and with illumination (light).

To study the interface properties between AZO and the B and P type layers, the *I-V* curves of the AZOonB and AZOonP devices were measured. From Figure 8.14(a) the resistance as estimated by the inverse of the gradients near the origin were  $2.2 \times 10^4$ ,  $8.0 \times 10^3$  and  $7.3 \times 10^3 \Omega$  (V/A) for the dark *I-V* before and after AI metallisation and light *I-V* after AI metallisation respectively. And from Figure 8.14(b) the resistance of the AZOonP device near the origin were  $2.7 \times 10^6$ ,  $1.2 \times 10^6$  and  $8.6 \times 10^5 \Omega$  (V/A) for the dark *I-V* before and after AI metallisation respectively. From both Figure 8.14(a) and (b) all the *I-V* curves are fairly linear which suggests that AZO produces a

good ohmic contact to the B and P type layers. Initially, it was thought that perhaps given that AZO is always an *n*-type semiconductor, a heterojunction may exist across the interface between AZO and the B doped bilayers. However, the doping concentration in the B bilayers is fairly high which results in a very high free carrier concentration (around  $2.6 \times 10^{19} \text{ cm}^{-3}$  from Chapter 6) and given that AZO is also heavily degenerately doped with a carrier concentration around  $4.85 \times 10^{20}$  cm<sup>-3</sup> it actually acts more as a metal. So the interface is probably similar to that of a metal and a degenerately doped semiconductor which in this case acts more as a non-rectifying ohmic contact rather than a Schottky diode. Another likely possibility is the large defect density at the surface interface as often encountered with heavily doped SRO/SiO<sub>2</sub> bilayer structures. The high defect density allows multiple states within the allowed bandgap of the Si NC SRO/SiO2 material right at the interface. The high defect density at the surface can interact with a large quantity of the charge provided by the metal which shields the semiconductor from the properties of the metal. Consequently, the semiconductor's band states may unavoidably align to a location relative to the surface states which are in turn pinned to the Fermi level (due to their high density), all without influence from the metal [287]. A possible method to create a Schottky diode still with the B or P layers would be to add a thin intermediate insulating layer to unpin the bands. Having ohmic contacts between AZO and the B and P type SRO/SiO<sub>2</sub> bilayers may not be discouraging as this allows the potential for other type of solar cell device structures such as a standard quartz substrate *p-i-n* with patterned AZO across the surface or a HIT [288] type device with thin Si NC bilayers stacked on top of a crystalline wafer with transparent conducting AZO as an intermediate conducting layer before the metal finger contacts.

### 8.4.4 Suns-Voc



**Figure 8.15.** Suns- $V_{OC}$  contact schemes. (a) From across the metal contacts or from the P doped *n*-type bilayers to the AZO. (b) From the P doped *n*-type to the B doped *p*-type bilayers in a previous sample where the bilayers were slight offset due to a misalignment in the mask.

Suns- $V_{OC}$  measurements were also performed on all 4 devices. Suns- $V_{OC}$  allows the measurement of the open-circuit voltage,  $V_{OC}$ , of a solar cell without the effect of series resistance and in turn can produce a pseudo light J-V curve using a separate reference cell to estimate the light-generated current. For both the AZO superstrate Si QD solar cell

devices which were contacted as shown in Figure 8.15(a), there was no  $V_{OC}$  response which is what is expected if the device is in fact heavily shunted. A previous earlier sample which had a slight offset between the *n* and *p* layers because the B and P SRO/SiO<sub>2</sub> bilayers were deposited separately due to a slight misalignment with the metal mask was also tested. When this device was probed between the *n* and *p* layers on the very edge of the device as shown in Figure 8.15(b), it produced a Suns-V<sub>OC</sub> of 93 mV. This suggested that the *n-i-p* regions in the devices still produced a rectifying junction although the V<sub>OC</sub> was much lower than expected due to the heavy shunting. From the ToF-SIMS results shown before, the B and P dopants seem to make a reasonable *n-i-p* junction but the AI that diffused into the P side is actually a deep *p-type* dopant for Si and typically used in *p*<sup>++</sup> back surface fields for c-Si solar cells. Perhaps there was still enough of a difference between the dopants to allow charge separation.



Pseudo light J-V curve

**Figure 8.16.** Suns- $V_{oc}$  pseudo light *J*-*V* curve of the superstrate Si QD *n-i-p* solar cell device when contacted on the edge between the n- and p- layers from a sample with a slightly offset.

The AZOonB and AZOonP were also measured. The AZOonB produced no response for the Suns- $V_{oc}$  measurements. However the more resistive AZOonP sample actually always produced a small voltage around 47 mV. This may suggest some form of small Schottky contact barrier due to a strong band misalignment between the *n*-type SRO/SiO<sub>2</sub> layer and the *n*-type AZO despite the ohmic *I*-*V* properties in the previous section.



**Figure 8.17.** Suns-V<sub>OC</sub> pseudo light *J*-V curve of the AZOonP sample.

# **8.5 Conclusion**

In summary, although this first demonstration of annealing Si QDs at 1100 °C together with a TCO did not produce a working photovoltaic device, it still provided information to arrive at interesting and useful conclusions. The most important observation is that the contact between AZO and the B and P doped SRO/SiO<sub>2</sub> bilayers is ohmic believed to be due to the high doping or defects at both interfaces. If it were not for the inter-diffusion during the annealing stage, it seems that this could have been an excellent TCO for single-junction Si QD solar cells. This ohmic property could allow for other types of devices to be created with Si NC materials. For alternative methods for utilising AZO for Si QD solar cells and optoelectronic devices refer to the section on "Scope for Future Work in the Field" in the next chapter.

# Chapter Nine: Conclusions, Original Contributions and Future Work

# 9.1 Conclusions

Third generation photovoltaic concepts [2-4] aim to increase the efficiency above that of the Shockley-Queisser limit [1], whilst reducing the material cost per unit area. This is the ultimate goal in the long term future of photovoltaics. Silicon is one of the most abundant elements in the Earth's crust and its benefits include low cost, non-toxicity and compatibility with the current photovoltaics industry. A tandem solar cell consisting of low cost Si based materials with different bandgaps is a promising method to reduce the thermalisation and below bandgap losses. By using the quantum confinement phenomenon, the bandgap of Si guantum dot (QD) or nanocrystal (NC) material can be adjusted to meet the required values for an optimal tandem cell. The beauty of Si QDs lies in this particular characteristic of bandgap tunability or bandgap engineering by varying their size and shape. Currently, the research focus on third generation all-Si nanostructure tandem solar cell has been on the actual Si NC material itself rather than implementing full tandem cells. Nevertheless, there has been research into various Si NC solar cell devices albeit the demonstrated efficiencies have been low. An important issue has been the heavy current crowding and series resistance of the solar cell devices. Therefore, aluminium zinc oxide (AZO), a common transparent conducting oxide (TCO) often used in thin-film solar cells, has been proposed as a possible candidate to use in Si NC solar cell devices. The biggest issue however is the high temperature annealing step (1100 °C) that is required in the formation of the Si NCs which would most likely be detrimental to the properties of the transparent conducting AZO. The main results of this thesis from the experimental Chapters 5-8 are summarised below.

Chapter 5 studies the utility of spherical aberration corrected high resolution transmission electron microscopy (HRTEM) with real-time *in situ* heating on Si NCs from phosphorus doped silicon rich oxide/silicon dioxide (SRO/SiO<sub>2</sub>) bilayers. The initial solid-state nucleation and formation of Si NCs were observed by an aberration-corrected FEI Titan 800-300 keV FEG S/TEM with a heating stage. The results showed that the shape of the

Si NCs were not spherical at least for moderate content Si in the SRO layers and the Si NCs were well confined within their layers at least for temperatures up to 600 °C. With further analysis some percolation threshold may be established in these Si NC films. Also, the results from this HRTEM study suggested that nucleation of the Si NCs begins at an unsuspectingly low temperature (450 °C), this was the temperature when Si(111) lattice fringes could be observed during the HRTEM imaging. This low temperature nucleation suggests that *ex situ* annealing at 1100 °C may not be necessary. However it was shown in the next chapter that this was not the case. Possible reasons for the differences between conventional furnace annealing versus heating stage annealing in the chamber of a HRTEM were discussed. This technique is promising for future study in the area of Si NCs.

Chapter 6 studies the use of high Si content SRO in magnetron sputtered SRO/SiO<sub>2</sub> bilayer superlattice thin films with boron (B) and phosphorus (P) doping. The stoichiometry was approximately SiO<sub>0.3</sub>, meaning that there were approximately three times as many Si atoms than O atoms in the SRO layers. Doping is also an important aspect for Si NC research because in order to make solar cell devices *p*-type and *n*-type material are required. Doping however also changes the structural, optical and electrical properties of these films. The dependence of annealing temperature on the Si NC with doping was first investigated by grazing incidence X-ray diffraction (GIXRD) and Raman spectroscopy. It was clearly established that conventional furnace annealing requires temperatures of at least 1100 °C for satisfactory Si NC formation contrary to the behaviour reported in the previous chapter when the SRO/SiO<sub>2</sub> films were annealed inside the chamber of an HRTEM.

Using the Scherrer equation, the GIXRD results showed that the high Si content created much larger average Si NC size. Furthermore, P doped samples resulted in the largest average size of  $11.1 \pm 2.2$  nm, followed by the B of  $9.6 \pm 2.0$  nm then intrinsic of  $9.1 \pm 2.4$  nm. The Raman spectroscopy results were also consistent with the GIXRD results which showed that the highest crystalline-to-amorphous Si fraction was found in the P doped samples, followed by the B and then the intrinsic. Through conventional HRTEM, it was observed that the intrinsic (undoped) samples maintained their SRO/SiO<sub>2</sub> bilayer structure after annealing at 1100 °C. However, the SRO and SiO<sub>2</sub> layers were intermixed after the annealing of both the B and P doped samples. Room temperature photoluminescence

showed that both the intrinsic and B doped samples had a peak at 1.48 eV however there was a strong red-shift for the P doped sample down to 1.32 eV which was attributed to the larger Si NC size and thus weaker quantum confinement. The intensity of the P was also 4.5 times higher than both the intrinsic and B doped samples which suggested a larger absorption capture cross-section. Finally, the Hall measurements showed strong decreases in resistivity for the doped samples down to 120  $\Omega$ cm for the P and a low 0.66  $\Omega$ cm for the B doped sample which opens new avenues for Si QD solar cell device structures.

Chapter 7 looks at the applicability of AZO as a TCO for Si QD solar cell devices. The high temperature furnace annealed properties of magnetron sputtered AZO thin films were studied. The initial preliminary experiment showed that the AZO films did not peel, decompose or evaporate even when annealed at 1100 °C in an inert gas atmosphere although their surface roughness did increase significantly. The AZO films also maintained their high optical transmission properties, but had their conductivity reduced by many orders of magnitude. The first main experiment in Chapter 7 investigated the temperature dependence of the AZO films when annealed in  $N_2$  and forming gas (4% H<sub>2</sub> / 96% N<sub>2</sub>). The forming gas reduced and decomposed the AZO films even at a low 500 °C. For the AZO films annealed in N<sub>2</sub> the increase in annealing temperature resulted in loss in carrier concentration which was indirectly shown through the optical transmission data. There was a reverse Burnstein-Moss effect shown by the red-shift in the absorption edge with increasing annealing temperature. Furthermore, there was an obvious increase in optical transmission in the infrared region due to the loss in free carrier absorption with increasing temperature. Both of these effects showed that the free carriers as a result of extrinsic Al dopants are lost due to the annealing. The most likely explanation was the chemisorption of oxygen on the surface of the thin film or oxygen trapped at defects such as grain boundaries or from the air if they were removed from the furnace at an insufficiently low temperature. XPS measurements showed that the AI still remained in the films even at 1100 °C rather than evaporate, which led to the conclusion that the AI becomes inactive after the annealing. Possible explanations include: Al diffuses or getters into grain boundaries or internal micro-pores where they are unable to act as a dopant. Formation of unwanted  $Al_2O_3$  was also a possibility.

In the final experiment in Chapter 7 it was discovered that annealing the furnace with forming gas prior to annealing AZO samples actually allows the AZO samples to partially retain their conductivity (approximately two to three orders of magnitude change from the as-deposited AZO samples). Removing the samples at a lower temperature (below 150 °C) from the furnace also reduces the loss in conductivity. The 'pre-forming gas' treatment may have removed any oxidising contaminants, perhaps oxides that may have caused unwanted chemisorption of oxygen from the surface of the AZO film. The final 1100 °C AZO films from this 'pre-forming gas' treatment had a best bulk resistivity of around 6.28 ×  $10^{-2} \,\Omega$ cm.

Chapter 8 combined the work from Chapter 6 and Chapter 7 to investigate a novel AZO superstrate *n-i-p* Si QD solar cell device design. A literature review survey of the different Si QD solar cell device designs was presented and the advantages and disadvantages behind each device design were discussed. A new solar cell device using AZO and Si NC from SRO/SiO<sub>2</sub> bilayers was proposed and then prototypes were fabricated. The AZO superstrate *n-i-p* Si QD solar cell device was deposited on quartz substrates so the photovoltaic activity could only be attributed to the Si NC layers compared to designs that involve depositing the Si NC layers on conducting substrates such as crystalline Si (c-Si) wafers or poly-Si thin films. It was shown from ToF-SIMS that there was heavy cross-diffusion of elements such as Al and Zn into the *n-i-p* region during the high temperature (1100 °C) annealing stage. *I-V* measurements on the devices showed linear rather than rectifying diode responses. The linear resistor like responses pointed to shunting of the *n-i-p* junction most likely due to the heavy cross-diffusion of Al and Zn.

In Chapter 8, AZO were deposited on annealed high Si content B and P doped SRO/SiO<sub>2</sub> bilayers. It was shown that the contact between the AZO and the B and P doped SRO/SiO<sub>2</sub> bilayers is ohmic, possibly due to the high doping or defects at both interfaces. Because the contacts were ohmic it may be possible to design other types of Si NC solar cell devices using AZO. Further ideas are discussed later in this chapter under Section 9.3 - Scope for Future Work in the Field.

# 9.2 Original Contributions to the Field and Their Significance

- Observed for the first time, the solid-state nucleation of silicon nanocrystals (Si NCs) in SRO/SiO2 bilayers in real time via an aberration corrected high resolution transmission electron microscope (HRTEM) with *in situ* heating up to 600 °C.
- 2) Investigated the dependence of annealing temperature up to 1100 °C on Si NC formation in SRO/SiO<sub>2</sub> bilayer superlattice thin films (although, similar experiments have been done for Si NCs from plasma enhanced chemical vapour deposition (PECVD) and for Si nitrides and carbides). It was shown that the higher the annealing temperature, the better the extent of crystallisation of the Si NCs.
- 7) Investigated the use and advantages of high Si content SRO in SRO/SiO<sub>2</sub> bilayer superlattice thin films used in the fabrication of Si NCs. High Si content SRO tends to produce thin films with lower resistivity and higher absorption cross-sections which are better properties for fabricating Si QD solar cell devices. The effects of boron and phosphorus doping on the properties of high Si content SRO/SiO<sub>2</sub> bilayers were also studied.
- 3) Investigated the structural, electrical and optical properties of transparent conducting aluminium doped zinc oxide (AZO) thin films annealed at temperatures up to 1100 °C. A special method was developed so that the thin film AZO samples could retain their conducting nature to within approximately 2 to 3 orders of magnitude after annealing in the absence of oxygen. This result may also have various applications outside of photovoltaics.
- Demonstrated that AZO forms a good ohmic contact to both the high Si content B and P doped SRO/SiO<sub>2</sub> bilayer superlattices.
- 5) Conceptualised the first Si QD/NC *n-i-p* superstrate configured solar cell using AZO as a transparent conducting layer. AZO is often used as a transparent conducting layer for thin-film amorphous Si and CIGS solar cells although AZO has never been

investigated in the device structure of Si NC solar cells due to the high temperature annealing step for Si NCs that is required.

# 9.3 Scope for Future Work in the Field

## 9.3.1 Improvement to the Si NC Material Towards an Ideal Si QD Matrix

Current Si QD material research has been focused on depositing bilayers of Si along with its dielectrics. This method was introduced by Zacharias *et al.* [53] with "good size and density control". However, in reality, the current Si QD material and structural is still very far from ideal. It was shown in Chapter 2 that due to the lack of periodicity, transport properties in Si QD matrices depend exponentially on the barrier width of the dielectric material (i.e. the distance between the QDs); the square root of the barrier height of the dielectric material; and the square root of the effective mass of the carrier. In terms of performance, the present physical structure of the Si QD material should have much:

- 1) narrower Si QD size distribution
- 2) closer and more evenly spaced Si QDs
- 3) more spherical Si QDs
- 4) lower barrier height (e.g. with other dielectric materials)
- 5) better passivated surfaces

If an "ideal Si QD matrix" were to be constructed it would most likely consist of perfect spherical Si QDs packed as closely as possible, that being in a face-centred cubic (FCC) or hexagonal close-packed (HCP) fashion. The volume of QD material (i.e. Si) in the matrix would therefore be 74.0%, with the remaining volume occupied by a dielectric material with a low barrier height. The diameter of the Si QD would need to be around 3.5-4 nm if a bandgap of 1.7-1.8 eV is desired. An "ideal Si QD matrix" in photovoltaic terms should translate to much better carrier lifetime and mobility, high absorption co-efficient

and lower device series resistance compared to the Si QD matrices being studied currently. At present, fabrication of an "ideal Si QD matrix" is still not possible as there are limitations to the technology available to engineer such intricate and precise structures down to the atomic scale. What should be done in the near future is modelling work through first principles (such as the work by Jiang and Green [37]) which may be a good starting point to access the true potential of such an "ideal Si QD matrix". If indeed an "ideal Si QD matrix" material is possible this may remove the need for a conducting substrate or TCO altogether.

# 9.3.2 Improvements on the AZO Conductivity with Temperature and Better Ways to Utilise AZO with the Si NC Material

Even though it was shown that the conductivity for AZO decreases by about 2 to 3 orders of magnitude even after using the special "pre-forming gas" method in Chapter 7, the resistance to decrease in conductivity can probably be improved. Possibilities include:

- 1) increasing the initial AI content of the AZO before annealing
- 2) depositing a protective layer on the surface before annealing
- 3) varying more annealing conditions such as gas flow or type of gas used
- 4) post-annealing in forming gas
- 5) using a different annealing method (see below)

In addition to furnace annealing, there are other types of annealing methods such as rapid thermal annealing (RTA), flash lamp annealing or laser annealing. All of these methods involve much higher annealing rates and lower thermal budgets which may be more beneficial to this transparent conducting AZO for superstrate Si QD solar cells concept. RTA of Si NCs has already been investigated by a few authors [273, 289] with comparable results to conventional furnace annealing. Laser annealing has been used for fabricating crystalline silicon on glass (CSG) technology by both solid and liquid phase crystallisation [290, 291]. Laser annealing was also briefly investigated by the author of this thesis using

an 808 nm diode laser on high content SRO/SiO<sub>2</sub> bilayers to form Si NCs although the results were so far unsuccessful. It seemed that the control of the laser power and thermal input to the SRO/SiO<sub>2</sub> bilayer samples needs to be very precise; an insufficient laser power and thermal input results in no formation of Si NCs and too much power results in the melting and thus intermixing of the layers which is also undesirable. Nevertheless, further research into other annealing methods may be beneficial for annealing the transparent conducting AZO superstrate Si QD solar cells.

Another interesting possibility is to use AZO or simply ZnO as the dielectric layer. Kuo *et al.* have demonstrated the formation of Si NCs embedded in ZnO by sputtered bilayers of amorphous Si (a-Si)/ZnO followed by rapid thermal annealing up to 1000 °C [292, 293]. The authors suggest that the carrier transport differs from that of traditional Si dielectric matrix materials. They believe that the transport through their Si NC/ZnO material is dominated by multistep tunnelling via the more conducting ZnO and thus the resistivity of their films is much lower than those deposited with SiO<sub>2</sub> matrices by about four orders of magnitude. The use of ZnO as a matrix for Si NCs leaves plenty of scope for future work in photovoltaics as well as optoelectronics in general.

#### 9.3.3 Si QD Solar Cell Devices in General

The open-circuit voltage of current Si QD photovoltaic devices still requires improvement. Currently, the best true Si QD solar cell, fabricated by Perez-Wurfl only has an open-circuit voltage of 493 mV [231], which, given its effective bandgap is, far from ideal. It is still in fact low compared to the open-circuit voltage of the most efficient crystalline Si (1.12 eV) HIT solar cell, by Panasonic at 740 mV [294] or the best thin-film a-Si solar cell at 896 mV [294]. Optimisation of certain aspects such as device shunting, doping, layer thicknesses and metal contacting should be further investigated. Hydrogen passivation of Si QD interface defects through methods such as doping with borane (BH<sub>3</sub>) or phosphine (PH<sub>3</sub>) or additional low temperature annealing in forming gas (Ar + H<sub>2</sub> mixture) may improve the V<sub>oc</sub> in the near future. Furthermore, if the current transport is improved the V<sub>oc</sub> should also be improved due to better light absorption/trapping, reduced resistances and improved carrier collection in the depletion region.

So far, Si QD materials have much lower minority carrier lifetime and mobility compared to bulk Si [77]. These are the two important factors that limit the efficiency of the singlejunction Si QD solar cell devices. It therefore makes sense to theoretically model the effect of carrier lifetime and mobility on efficiency and to show that it is possible to achieve conversion efficiencies greater than at least about 15% if they are to be used in a tandem solar cell. For a 2-cell tandem with c-Si as the bottom cell, an optimum bandgap of approximately 1.7 to 1.8 eV is required [18]. In this case, according to the calculation by White et al. [295], in order to reach efficiencies greater than 30%, the top cell must have an efficiency of at least 18%. Some modelling work on estimating the highest achievable efficiencies with limited carrier lifetime and mobility has already been investigated by our third generation all-Si nanostructure tandem cell group [296]. It was shown that to achieve over 15% efficiency for a Si QD tandem cell with a 1.6 eV Si QD top sub-cell and a 1.12 eV crystalline Si bottom cell, carrier mobility larger than 1 cm<sup>2</sup>/Vs and a lifetime of at least 1 µs is required. For a lower mobility, a higher lifetime is required to reach the same efficiency and vice versa. In terms of actual Si QD solar cells, series resistance is another important limiting factor and it was also shown that series resistance becomes limiting once it increases above  $10^{-2} \Omega m^2$ .

In terms of actual tandem cells, a mechanically stacked Si QD tandem cell was demonstrated by our third generation all-Si nanostructure tandem cell group here at the University of New South Wales [297]. The mechanically stacked series connected tandem cell consisted of a lift-off [232] Si QD solar cell with a bandgap of 1.4 eV on top of a comparatively much more efficient thin-film polycrystalline Si solar cell. The open-circuit voltage was close to the sum of the two sub-cells whereas the short-circuit current was higher than even the top limiting Si QD sub-cell by itself. The improved short-circuit current was due to the higher current from the bottom thin-film polycrystalline Si cell which boosted the current of the top Si QD sub-cell causing the top-cell to actually operate in the reverse bias condition. Overall, the open-circuit voltage and short-circuit current of the tandem cell were not very impressive and this further stresses the importance of improving the efficiency of the single-junction Si QD solar cells.

#### 9.3.4 Other Areas of Research for Si QD Materials

SiO<sub>2</sub> is not the only dielectric material that can be used to confine Si QDs. Si<sub>3</sub>N<sub>4</sub> and SiC are also possible candidate dielectric materials for this purpose. Both of these dielectric materials have lower bandgaps than SiO<sub>2</sub> which would suggest better tunnelling probability, hence current transport would be greater for superlattice structures consisting of these materials. Many experimental studies on Si QDs in Si<sub>3</sub>N<sub>4</sub> [228, 298-302], SiO<sub>x</sub>N<sub>y</sub> [219, 303] and even hybrid SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> bilayers [304] either by PECVD [219, 300-303] or sputtering [228, 298, 299, 304] have already been demonstrated. Si<sub>3</sub>N<sub>4</sub> tends to constrain the growth of the Si NCs more effectively [228] than SiO<sub>2</sub> due its higher stiffness and density. SiC have also gained some attention in other studies by PECVD [277, 305, 306] and sputtering [225, 289, 307, 308], although for SiC the formation of  $\beta$ -SiC NCs hinders the formation of Si QDs and decreases their size and density. Another problem encountered with SiC is the potential current leakage across the SiC grain boundary traps which decrease the shunt resistance of the solar cell.

Germanium [309, 310] and other group IV elements are possible candidates for future research in QDs and QWs. Compared to Si, Ge has smaller electron and hole masses and a greater dielectric constant. In addition, its exciton Bohr radius is 24.3 nm [310] compared to Si at only 4.9 nm [311]. This means that larger Ge QDs can produce the same quantum confinement effect making the size of the QDs less stringent and thus bandgap can be more easily controlled. And finally Ge has a lower melting point (approximately 938.3 °C) than Si making it more advantageous for designing QD solar cell devices and especially with AZO. The main disadvantage of Ge is that it is much less abundant than Si so is unlikely to be used in long term mass manufacturing of solar cells.

More recently some research effort has involved fabrication of free-standing colloidal [312] (solution based) Si QDs through many various pathways, such as non-thermal plasma synthesis [284, 313, 314], high temperature decomposition of hydrogen silsesquioxane (HSQ) [315, 316], high temperature annealing of SiO<sub>x</sub> powders [317], controlled oxidation of mechanically milled Si [318, 319] or solution reduction of SiCl<sub>4</sub> [320]. Most of these synthesis pathways require a final dry or wet (using HF) etch to either remove the SiO<sub>2</sub> shell or reduce the Si nanocrystal size. Colloidal Si NCs show similar quantum confinement effects as solid-state Si NCs embedded in SiO<sub>2</sub> or other Si based dielectrics.

In terms of applications for optoelectronics, colloidal Si QDs may provide promising methods for making solar cell devices, as well as better simplicity, cost-effectiveness and scalability.
### **List of Author's Publications**

#### **A. Journal Publications:**

- T. C. J. Yang, Y. Kauffmann, L. Wu, Z. Lin, X. Jia, B. Puthen-Veettil, T. Zhang, G. Conibeer, I. Perez-Wurfl, and A. Rothschild, "In-situ high resolution transmission electron microscopy observation of silicon nanocrystal nucleation in a SiO2 bilayered matrix," Applied Physics Letters, vol. 105, p. 053116, 2014.
- L. Wu, B. Puthen-Veettil, K. Nomoto, X. Hao, X. Jia, Z. Lin, T. C. Yang, T. Zhang, S. Gutsch, G. Conibeer, and I. Perez-Wurfl, "Temperature dependent electroluminescence from all-Si-nanocrystal p-i-n diodes grown on dielectric substrates," Journal of Applied Physics, vol. 119, p. 063102, 2016.
- T. Zhang, B. Puthen-Veettil, L. Wu, X. Jia, Z. Lin, T. C.-J. Yang, G. Conibeer, and I. Perez-Wurfl, "Determination of active doping in highly resistive boron doped silicon nanocrystals embedded in SiO2 by capacitance voltage measurement on inverted metal oxide semiconductor structure," Journal of Applied Physics, vol. 118, p. 154305, 2015.
- 4) Z. Lin, L. Wu, X. Jia, T. Zhang, B. Puthen-Veettil, T. C.-J. Yang, G. Conibeer, and I. Perez-Wurfl, "Boron doped Si rich oxide/SiO2 and silicon rich nitride/SiNx bilayers on molybdenum-fused silica substrates for vertically structured Si quantum dot solar cells," Journal of Applied Physics, vol. 118, p. 045303, 2015.
- X. Jia, L. Wu, Z. Lin, T. Zhang, T. C.-J. Yang, H. Xia, B. Puthen-Veettil, G. Conibeer, and I. Perez-Wurfl, "Characterization and simulation of optical absorption in Si nanocrystals," physica status solidi (c), vol. 12, pp. 271-274, 2015.
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#### **B. Conference Proceedings:**

- 8) T. C.-J. Yang, K. Nomoto, Z. Lin, L. Wu, B. Puthen-Veettil, T. Zhang, X. Jia, G. Conibeer, and I. Perez-Wurfl, "High Si Content SRO/SiO2 Bilayer Superlattices with Boron and Phosphorus doping for Next Generation Si Quantum Dot Photovoltaics," in 42nd IEEE Photovoltaic Specialists Conference, New Orleans, 2015.
- 9) T. C.-J. Yang, R. Lin, Z. Lin, T. Zhang, L. Wu, X. Jia, B. Puthen-Veetil, I. Perez-Wurfl, and G. J. Conibeer, "Investigation into High Temperature Post-Annealing of ZnO:Al as a Prospective Transparent Conductive Oxide Window Layer for Superstrate Silicon Nanostructure Solar Cells," in 29th European Photovoltaic Solar Energy Conference and Exhibition, Amsterdam, The Netherlands, 2014, pp. 284 - 290.
- 10) L. Wu, I. Perez-Wurfl, Z. Lin, X. Jia, T. Zhang, B. Puthen-Veettil, T. C.-J. Yang, H. Xia, and G. Conibeer, "Investigation on the effects of phosphine doping in Si nanocrystal material," in Proc. 40th IEEE Photovoltaic Spec. Conf., 2014, pp. 0666-0668.
- 11) T. Zhang, I. Perez-Wurfl, B. Puthen-Veettil, L. Wu, X. Jia, Z. Lin, T. C.-J. Yang, and G. Conibeer, "Capacitance-Voltage characterization of in-situ Boron doped silicon quantum dot in silicon dioxide," in Proc. 40th IEEE Photovoltaic Spec. Conf., 2014, pp. 1115-1118.

## **List of Tables**

Table 2.1. Results of the material properties extracted by C-V measurements of B and P doped SRO/SiO <sub>2</sub> superlattices in a MOS structure [77]	່ງ 25
Table 3.1. Basic structural, physical and optical properties of zinc oxide	35
Table 3.2. Basic electrical properties of zinc oxide	41
Table 6.1. GIXRD Si NC size and volume estimates	81
Table 6.2. 4-PP and Hall measurements	90
Table 6.3. Summary of the properties between intrinsic, B and P doped SRO/SiO <sub>2</sub> bilayers	92
Table 7.1. Literature survey of RF magnetron sputtered AZO films	95
Table 7.2. Preliminary experiment parameters and results	103
Table 7.3. Annealing temperature and gases	105
Table 7.4. Four-point probe resistivity measurement results	107
Table 7.5. Hall Effect measurement results	108
Table 7.6. RMS surface roughness of the 150 W RF magnetron sputtered AZOsamples under various post annealing treatments	112
Table 7.7. 4-PP and Hall measurements	119
Table 8.1. List of various Si QD photovoltaic devices from literature.	124

# List of Figures and Illustrations

Figure 1.1. Efficiency & cost projections of 1 <sup>st</sup> (I), 2 <sup>nd</sup> (II) and 3 <sup>rd</sup> (III) generation PV technologies [2] (2003)	I
Figure 1.2. Energy band diagram displaying the main energy loss mechanisms: 1) non- absorption due to photons with insufficient energy (i.e. energy below the bandgap); 2) thermalisation of photogenerated carriers; 3-4) contact and junction losses; 5) recombination loss [2]	2
Figure 1.3. Multiple bandgap concepts: (a) spectrum splitting; (b) tandem cell [4]. A combination of both concepts is also feasible	3
Figure 1.4. A theoretical design of an all-Si tandem cell using quantum confined QDs [19]	5
Figure 2.1. Bulk band alignments between crystalline Si (c-Si) and its corresponding oxides (SiO <sub>2</sub> ), nitrides (Si <sub>3</sub> N <sub>4</sub> ) and carbides (SiC) [18]	3
Figure 2.2. Superlattice bilayered structure illustrating the nucleation of Si QDs in a "Silicon Rich Oxide" (SRO or SiOx) layer [18]	5
Figure 2.3. Normalised PL spectra displaying a definitive blue-shift concurrent with the NC diameter [53]	7
<ul> <li>Figure 2.4. TEM images of cross-sectional annealed SRO/SiO<sub>2</sub> specimens: (a) SiO<sub>1.30</sub>/SiO<sub>2</sub> multiple bilayers (b) SiO<sub>1.30</sub>/SiO<sub>2</sub> multiple bilayers at higher magnification (c) SiO<sub>1.00</sub>/SiO<sub>2</sub> multiple bilayers (d) SiO<sub>1.00</sub>/SiO<sub>2</sub> multiple bilayers at higher magnification (e) SiO<sub>0.86</sub>/SiO<sub>2</sub> multiple bilayers (f) SiO<sub>0.86</sub>/SiO<sub>2</sub> multiple bilayers at higher magnification [60].</li> </ul>	)
Figure 2.5. Formation energy of dopant atoms of (a) B and (b) P placed substitutionally at the centre of a Si nanocluster as a function of inverse NC radius. The shapes (filled square, empty square and empty triangle) represent different modelling regimes [66]	l
<ul> <li>Figure 2.6. (a) Location of the dopant impurity within the Si nanocluster as it moves along two separate paths to the surface (b) The formation energy of the dopant impurity versus the distance from the central location (marked by the numbers 1-6) [66]</li></ul>	3
Figure 2.7. (a) Resistance versus B dopant concentration in 4 nm SRO/6 nm SiO <sub>2</sub> superlattices (15-bilayers) on quartz measured by TLM [63, 70]. (b) Resistance versus P dopant concentration in 5 nm SRO/6 nm SiO <sub>2</sub> superlattices (15-bilayers) on quartz measured by TLM [71]	1

Figu	re 2.8. Schematic illustration of two different mechanisms. (a) Doping of the dielectric a-SiO <sub>2</sub> material surround the Si QD with an abrupt transition. (b) Doping of the amorphous sub-oxide region surrounding the Si QD [63]
Figu	are 3.1. Schematic diagram of a typical amorphous silicon (a-Si) solar cell illustrating the necessity of TCOs for thin-film solar cells. Typical values for the thicknesses are given for each layer
Figu	ure 3.2. (a) Primitive cell and hexagonal prism of wurtzite structured ZnO lattice, where <i>a</i> and <i>c</i> are lattice constants. (b) Schematic drawing of a single crystal hexagonal prism showing the different surface planes ( <i>a</i> -, <i>r</i> - and <i>c</i> -) and crystallographic orientations [104]
Figu	are 3.3. Band alignment diagram for II-VI semiconductors derived using the density functional theory (DFT) calculations by Wei and Zunger [113]. The ZnS valence band maximum energy has been arbitrarily set to 0 eV [114]
Figu	ure 3.4. Defect formation energy for common ZnO defects as a function of Fermi level calculated via the first-principles pseudopotential method by Kohan <i>et al.</i> [124]. The graph on the left (a), is for high and on the right (b), for low zinc partial pressure. The 0-axis of the Fermi level is fixed at the top of the valence band
Figu	ure 3.5. (a) mobilities and (b) resistivities of various doped and intrinsic ZnO thin films vs. the carrier concentration compiled by Ellmer in Refs. [143, 144] and references therein. The thin films were deposited by various methods including: magnetron sputtering (all squares), MOCVD (open diamond) and PLD (open circle). The different lines represent different theoretical estimations
Figu	are 4.1. Schematic diagram of a typical RF magnetron sputtering system
Figu	are 4.2. 4-PP sheet resistivity measurement of the <i>n-p</i> solar cell [198]
Figu	are 5.1. Bright-field TEM micrograph of the as-deposited <i>n</i> -type phosphorous doped SRO/SiO <sub>2</sub> bilayers of the <i>p-i-n</i> sample on a silicon substrate at room temperature 67
Figu	re 5.2. <i>In situ</i> HRTEM micrograph of the <i>p-i-n</i> specimen at 400 °C
Figu	are 5.3. <i>In situ</i> HRTEM micrograph of the <i>p-i-n</i> specimen at 450 °C
Figu	are 5.4. <i>In situ</i> HRTEM micrograph of the <i>p-i-n</i> sample after 15 min at 500 °C
Figu	are 5.5. <i>In situ</i> HRTEM micrograph of the <i>p-i-n</i> sample after 40 min at 500 °C and 10 min at 600 °C
Figu	are 6.1. GIXRD patterns of (a) intrinsic, (b) boron and (c) phosphorus doped high Si content SRO/SiO <sub>2</sub> bilayered thin films on quartz substrates annealed at various temperatures for 1 hour in a 1 L quartz tube furnace with a $N_2$ flow rate of 2.5 L/min

Figure 6.2. GIXRD patterns of the 1100 °C annealed intrinsic, B and P doped SRO/SiO2 bilayer thin films on quartz substrates (a) full range and (b) with a separate higher resolution scan near range of the Si(111) peaks
Figure 6.3. (a) Bright-field HRTEM and (b) corresponding EFTEM image of annealed intrinsic SRO/SiO2 bilayers under a magnification of 800,000×
Figure 6.4. (a) Bright-field HRTEM and (b) corresponding EFTEM image of annealed B doped SRO/SiO <sub>2</sub> bilayers under a magnification of 500,000×
Figure 6.5. (a) Bright-field HRTEM and (b) corresponding EFTEM image of annealed P doped SRO/SiO <sub>2</sub> bilayers under a magnification of 500,000×
<ul> <li>Figure 6.6. Absolute Raman spectra of the (a) intrinsic, (b) B and (c) P doped</li> <li>SRO/SiO<sub>2</sub> bilayers on quartz substrates with annealing temperature up to 1100</li> <li>°C. A normalised c-Si reference from a c-Si wafer is included as a guide</li></ul>
<ul> <li>Figure 6.7. (a) Normalized Raman spectra of the annealed intrinsic, B and P doped SRO/SiO<sub>2</sub> bilayers on quartz substrates as well as the spectrum from a reference c-Si wafer. (b) Example of the peak fitting for the B doped sample</li></ul>
Figure 6.8. Normalized RT PL spectra of the intrinsic, B and P doped SRO/SiO2 bilayer samples on quartz substrates
Figure 7.1. Transmittance vs. wavelength of RFMS AZO ( $T_{sub}$ = 200 °C ) films on Corning glass substrates with different AI content [147]
Figure 7.2. Transmission of RF magnetron sputtered as-deposited and 1100 °C annealed ZnO and AZO films
Figure 7.3. AFM images of a) ZnO, b) AZO, c) annealed ZnO and d) 1100 °C annealed ZnO:AI thin films showing the surface roughness
Figure 7.4. Transmission spectra of the AZO thin films annealed at different temperatures with $N_2$ in a 1 L furnace
Figure 7.5. Transmission spectra of the AZO thin films annealed at different temperatures with forming gas in a large tube furnace
Figure 7.6. GIXRD patterns of the AZO thin films annealed at different temperatures with $N_2$ in a 1 L furnace
Figure 7.7. GIXRD patterns of the AZO thin films annealed at different temperatures with forming gas in a large tube furnace. Note, the 700 °C and 800 °C are not shown here as the film completely decomposes after this temperature
Figure 7.8. SEM image of surface of the AZO sample annealed at 1000 °C in $N_2$ 111
Figure 7.9. Column graph of the atomic percentage of the major elemental species in the annealed AZO films as analysed by XPS

Figure 7.10. Transmission spectra of the 100 W AZO thin films annealed at different temperatures with $N_2$ in a 1 L furnace with pre-forming gas treatment of the quartz tube	5
Figure 7.11. $\Psi$ values obtained by WVASE for as-deposited AZO on a Si wafer and its best fitting	7
Figure 7.12. <i>Δ</i> values obtained by WVASE for as-deposited AZO on a Si wafer and its best fitting	7
Figure 7.13. Optical constants for the as-deposited AZO thin film	8
Figure 8.1 Schematic diagram of an interdigitated Si QDs in SiO <sub>2</sub> superlattice mesas structure photovoltaic device [209]	6
Figure 8.2. Schematic diagram of Si QDs in SiC superlattice photovoltaic device structure [274]	7
Figure 8.3. Schematic diagram of the Si QD in SiC photovoltaic membrane device. The grey areas represent insulation layers separating the active regions from the c-Si wafer [277]	8
Figure 8.4. Schematic diagram of a heterojunction photovoltaic device consisting of an <i>n</i> -type Si QD/SiO <sub>2</sub> bilayered superlattice on a <i>p</i> -type Si wafer with Al contacts (not to scale) [280]	9
Figure 8.5. Schematic diagram of a colloidal Si QD Schottky photovoltaic device [283]. 13	0
Figure 8.6. Schematic diagram of the final superstrate <i>n-i-p</i> Si QD solar cell device structure	2
Figure 8.7. Image of the metallic mask used in the sputtering of the <i>n-i-p</i> regions of the superstrate Si QD solar cell device	4
Figure 8.8. Photographs of the final AZO superstrate <i>n-i-p</i> Si QD solar cell device structure before (a) and after (b) AI metallisation	5
Figure 8.9. Schematic diagram of the final superstrate AZOonB and AZOonP device structure	5
Figure 8.10. Photographs of the final AZO on B (left) and P (right) 20 high Si content SRO/SiO <sub>2</sub> bilayer devices before (a) and after (b) AI metallisation	7
Figure 8.11. Optical microscopy image of the sputter and analysis area after the ToF- SIMS depth profile measurement of the AZO superstrate <i>n-i-p</i> solar cell device before AI metallisation (top left), elemental maps of the analysis area (bottom) and the elemental maps side by side to the analysis area (top right)	8
Figure 8.12. ToF-SIMS depth profile of the AZO superstrate <i>n-i-p</i> solar cell device 14	0

Figure 8.13. <i>I-V</i> curves of the AZO superstrate <i>n-i-p</i> solar cell devices in the dark before and after AI metallisation and with illumination (light). HF dip using (a) tape and (b) photolithography.	143
Figure 8.14. <i>I-V</i> curves of the AZO on (a) B and (b) P devices in the dark before and after AI metallisation and with illumination (light).	144
Figure 8.15. Suns- $V_{OC}$ contact schemes. (a) From across the metal contacts or from the P doped <i>n</i> -type bilayers to the AZO. (b) From the P doped <i>n</i> -type to the B doped <i>p</i> -type bilayers in a previous sample where the bilayers were slight offset due to a misalignment in the mask.	146
Figure 8.16. <i>Suns-V<sub>oc</sub></i> pseudo light <i>J-V</i> curve of the superstrate Si QD <i>n-i-p</i> solar cell device when contacted on the edge between the n- and p- layers from a sample with a slightly offset.	147
Figure 8.17. Suns-Voc pseudo light J-V curve of the AZOonP sample	148

# List of Symbols, Abbreviations and Nomenclature

#### A. Symbols and Physical Properties:

Symbol	Definition
a	Quantum dot diameter
Α	Absorption
Å	Angstrom
at.	Atomic
a.u.	Arbitrary units
BE	Binding energy
β	Line broadening at half maximum; or full width at half maximum
	(FWHM)
$C_S$	Spherical aberration correction
°C	Degrees Celsius
\$	Dollar
d	Diameter of a spherical quantum dot; inter atomic spacing; or
	spacing between diffraction planes
$\delta_{rms}$	Surface roughness
Δ	Delta
eV	Electronvolt
$\underline{e_s}$	Static dielectric constant
<i>e</i> <sub>0</sub>	
<i>E</i> <sub>1</sub>	First quantised ground state energy
$E_{binding}$	Binding energy
E <sub>c</sub>	Energy of the conduction band edge
$E_c - E_d$	Donor level
$\Delta E_d$	Change in total energy; or change in total energy for one mole of
	a defect
$E_g$	Bandgap

$\Delta E_n$	Increase in energy for the <i>n</i> th confinement level
$E_p^a$	<i>p</i> -orbital energies of the anion
$E_p^c$	<i>p</i> -orbital energies of the cation
$E_{photon}$	Photon energy
$E_{ph}(\lambda)$	Energy of the photons at a specific wavelength $\lambda$
$E_{v}$	Energy of the valence band edge
$\Delta f$	Change in defocus
FF	Fill factor
g	Grams
$G_d$	Formation energy for one mole of a defect
h	Planck's constant
ħ	Reduced Planck's constant
hr	Hour
hv	Photon energy
$\Delta H_f$	Free energy of formation
Ι	Current
I <sub>0</sub>	Dark saturation current
Ia	Integrated intensity of the amorphous peak
I <sub>c</sub>	Integrated intensity of the crystalline peak
$I_{light}(\lambda)$	Short-circuit current at a specific wavelength $\lambda$
I <sub>MP</sub>	Maximum current
I <sub>SC</sub>	Short-circuit current
$I_T$	Total integrated area under the EELS spectrum
$I_{ZLP}$	Total area under the zero-loss peak
J	Joule
J'01	Reverse saturation current density of the diode 1
J'02	Reverse saturation current density of the diode 2
$J_L$	Light generated current density
J <sub>sc</sub>	Short-circuit current density
k	Boltzmann's constant; or wave-vector/function of a particle
Κ	Kelvin; or dimensionless shape factor
KE	Kinetic energy

$\underline{kT}$	Thermal voltage
q	
L	Litre; Average crystallite/grain size
λ	Wavelength
$m_0$	Electron rest mass
$m^*$	Effective mass of a particle
$m_e$	Free electron mass
$m_e^*$	Effective electron mass
$m_h^*$	Effective hole mass
min	Minute
mol	Mole
μ	Carrier mobility
n	Electron density; or ideality factor; or an integer
n <sub>e</sub>	Free electron concentration; or electron flux per second flowing
	through the external circuit at short-circuit conditions
$n_i$	Confined energy level
$n_{ph}$	Photon flux at a wavelength $\lambda$ incident on the solar cell per
	second
Ν	Carrier concentration
N <sub>C</sub>	Effective conduction band density of states
N <sub>d</sub>	Concentration of defects
N <sub>sites</sub>	Concentration of available defect sites
η	Efficiency
Ω	Ohm
π	Pi
%	Percent
ррт	Parts per million
PCE	Percentage conversion efficiency
P <sub>in</sub>	Power of the incident light on the solar cell
$P_{max}$	Maximum power
$P_{mono}(\lambda)$	Power of the incident light beam at a specific wavelength $\lambda$
I	Parallel
<b>上</b>	Perpendicular

$\Psi$	Psi
q	Elementary electronic charge
$q_{max}$	Contrast transfer function cut-off
R	Reflection; or nanocluster radius
Rad	Radian
$R_p$	Fresnel reflection coefficient for <i>p</i> - polarised light
R <sub>s</sub>	Fresnel reflection coefficient for s- polarised light
R <sub>Shunt</sub>	Shunt resistance
ρ	Resistivity; ratio between the Fresnel reflection coefficients for p-
	and s-polarised light
$ ho_{\Box}$	Sheet resistivity
S	Second
$\Delta S$	Change in vibrational entropy for one mole of a defect
σ	Conductivity
	Square
t	Thickness of a thin film
Т	Temperature; or transmission
T <sub>e</sub>	Electron tunnelling probability
T <sub>sub</sub>	Substrate temperature during sputtering
θ	Angle
v	Frequency
V	Voltage
V <sub>OC</sub>	Open-circuit voltage
$V_0$	Confinement barrier height
V <sub>max</sub>	Maximum voltage
$\phi$	Work function
x <sub>nc</sub>	$\frac{I_c}{(I_c + I_a)}$
y	Integrated Raman cross-section for c-Si to a-Si

#### **B. Materials and Devices:**

Symbol

Definition

a-Si	Amorphous silicon
a-Si:H	Hydrogenated amorphous silicon
a-Si₃N₄	Amorphous silicon nitride
a-SiC	Amorphous silicon carbide
a-SiC:H	Hydrogenated amorphous silicon carbide
a-SiO <sub>2</sub>	Amorphous silicon dioxide
AI	Aluminium
Ag	Silver
Ar	Argon gas
Ar <sup>+</sup>	Argon ion
ARC	Anti-reflection coating
AZO	Aluminium doped zinc oxide
В	Boron
BH <sub>3</sub>	Borane
c-Si	Crystalline silicon
CIGS	Copper indium gallium (di)selenide
Cu	Copper
FG	Forming gas (A small percentage of $H_2$ gas mixed with either Ar
	or N <sub>2</sub> )
FTO	Fluorine doped tin oxide
Ga	Gallium
$H_2O_2$	Hydrogen peroxide
$H_2SO_4$	Sulphuric acid
HF	Hydrofluoric acid
HSQ	Hydrogen silsesquioxane
i	Intrinsic
ITO	Indium tin oxide
In <sub>2</sub> O <sub>3</sub> :Sn	Tin doped indium oxide
LED	Light emitting diodes
MOS	Metal oxide semiconductor
µc-Si	Microcrystalline-silicon
n	N-type
N <sub>2</sub>	Nitrogen gas

NC	Nanocrystal
0	Oxygen
O <sub>2</sub>	Oxygen gas
Oi	Oxygen interstitial
O <sub>Zn</sub>	Oxygen zinc anti-site
р	P-type
Ρ	Phosphorus
$P_2O_5$	Phosphorus pentoxide
PH <sub>3</sub>	Phosphine gas
Piranha solution	3:1 ratio of 96% $H_2SO_4$ to 30% $H_2O_2$
QD	Quantum dot
QDSL	Quantum dot superlattice
QR	Quantum wire
QW	Quantum well
Si	Silicon
Si <sub>3</sub> N <sub>4</sub>	Silicon nitride
SiC	Silicon carbide
SiO <sub>2</sub>	Silicon dioxide
SiO <sub>x</sub>	Silicon rich oxide
SiO <sub>x</sub> N <sub>y</sub>	Silicon oxynitride
SL	Superlattice
SnO <sub>2</sub> :F	Fluorine doped tin oxide
SRO	Silicon rich oxide
ТСО	Transparent conducting oxide
Vo	Oxygen vacancy
V <sub>Zn</sub>	Zinc vacancy
Zn	Zinc
Zn <sub>i</sub>	Zinc interstitial
Zno	Zinc oxygen anti-site
ZnO	Zinc oxide
ZnO:Al	Aluminium doped zinc oxide
ZnS	Zinc Sulphide

## C. Fabrication and Characterisation Techniques:

Symbol	Definition
4-PP	Four-point probe
AFM	Atom force microscopy
APT	Atom probe tomography
CCD	Charged-couple device
C-V	Capacitance-voltage
EDS	Energy dispersive x-ray spectroscopy
EELS	Electron energy loss spectroscopy
EFTEM	Energy filtered transmission electron microscopy
EPR	Electron paramagnetic resonance
ESCA	Electron spectroscopy for chemical analysis
FEG	Field emission gun
FE-SEM	Field-emission scanning electron microscope
FIB	Focused ion beam
GIXRD	Grazing or glancing incidence x-ray diffraction
HREELS	High resolution electron energy loss spectroscopy
HRTEM	High resolution transmission electron microscopy
I-V	Current-voltage
LaB6	Lanthanum hexaboride
MOCVD	Metalorganic chemical vapour deposition
MOVPE	Metalorganic vapour phase epitaxy
MRD	Materials Research Diffractometer
PDS	Photothermal deflection spectroscopy
PECVD	Plasma enhanced chemical vapour deposition
PL	Photoluminescence
PLD	Pulsed laser deposition
PVD	Physical vapour deposition
RF	Radio frequency
RFMS	Radio frequency magnetron sputtering
RBS	Rutherford back-scattering spectroscopy
RTA	Rapid thermal annealing

SE	Spectroscopic ellipsometry
SEM	Scanning electron microscopy
SIMS	Secondary ion mass spectrometry
SPC	Solid phase crystallisation
SR	Spectral response
S/TEM	Scanning transmission electron microscope
TEM	Transmission electron microscopy
TLM	Transmission line measurement or transfer length measurement
ToF-SIMS	Time-of-Flight secondary ion mass spectrometry
VASE	Variable angle spectroscopic ellipsometer
WVASE	Woollam variable angle spectroscopic ellipsometer
XPS	X-ray photoelectron spectroscopy

#### D. Miscellaneous:

Symbol	Definition
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AISEF	Australian Israel Scientific Exchange Foundation
APA	Australian Postgraduate Award
ARENA	Australian Renewable Energy Agency
DFT	Density functional theory
EQE	External quantum efficiency
EMA	Effective mass approximation
FCC	Face-centred cubic
FWHM	full width at half maximum
HCP	Hexagonal close-packed
IQE	Internal quantum efficiency
IR	Infrared
LCAO	Linear combination of atomic orbitals
NIR	Near infrared
RMS	Root mean squared

RT	Room temperature
SPREE	School of Photovoltaic and Renewable Energy Engineering
ТЕТВ	Tyree Energy Technologies Building
T-L	Tauc-Lorentz
UNSW	University of New South Wales
UV	Ultraviolet
Vis	Visible

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