

## PECVD Fabrication, Electrical Characterization and Laser Dopant Activation of Silicon Nanocrystals

**Author:** Zhang, Tian

**Publication Date:** 2016

DOI: https://doi.org/10.26190/unsworks/19589

## License:

https://creativecommons.org/licenses/by-nc-nd/3.0/au/ Link to license to see what you are allowed to do with this resource.

Downloaded from http://hdl.handle.net/1959.4/57648 in https:// unsworks.unsw.edu.au on 2024-05-03

# PECVD Fabrication, Electrical Characterization and Laser Dopant Activation of Silicon Nanocrystals

Tian Zhang

A THESIS IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY



School of Photovoltaic and Renewable Engineering

Faculty of Engineering

May 2016

PLEASE TYPE		THE UNIVERSITY OF NEW Thesis/Dissertati	V SOUTH WALES on Sheet
Surname or Family name:	Zhang		
First name:	Tian	Other na	me/s:
Abbreviation for degree as g	iven in the Universit	y calendar: PHD	
School: School of Photo	voltaic and Ren	ewable Energy Faculty:	Engineering
	n Electrical Ch	aracterization and Laser	Dopant Activation of Silicon Nanocrystals

#### Abstract 350 words maximum: (PLEASE TYPE)

This thesis presents insights into the electrical properties of doped silicon nanocrystals (ncSi) for 3rd generation photovoltaic solar cells. While investigating doping of PECVD ncSi-based PV devices (Chapter 3), it has become clear that commonly used techniques to dope and characterise these ncSi films are not effective. In view of this, specially designed structures for Capacitance-Voltage (CV) measurements and pulsed laser annealing techniques have been developed to characterise the doping effects and improve doping efficiency, respectively. Two first-author journal papers have been published based on the work presented in Chapter 4 and Chapter 5 of this thesis. Chapter 4 presents the research about CV measurements and evaluations of electrically active boron doping concentrations in ncSi. The work about improved dopants (Boron and Phosphorus) activation in ncSi by pulsed KrF laser is mainly included in Chapter 5. The characterization and fabrication techniques also presented in this thesis have assisted other journal publications on the research of doped ncSi material, ncSi-based photovoltaic devices and renewable energy applications.

The two most important contributions of this thesis are:

1. The demonstration of an inverted MOS structure to measure doping using CV measurements and

2. The improvement of the conductivity of ncSi films using a pulsed KrF excimer laser after the crystal growth.

This thesis starts with the investigation of plasma-enhanced chemical vapour deposition (PECVD) for fabricating silicon nanocrystals along with boron (B) and phosphorus (P) doping. The material properties of non-stoichiometric silicon oxide before and after annealing and the B/P doped ncSi are investigated. After the demonstration of ncSi preparation and doping by PECVD, ncSi-based photovoltaic devices were eventually fabricated and analysed. The devices showed diode I-V characteristics and an open-circuit voltage of 230 mV was achieved. However, the parameters extracted from electrical measurements indicated severe limitations due to low carrier transport and strong non-radiative recombination. These limiting factors can be attributed to the ineffective doping in ncSi, which is a general problem for nanostructured semiconductor materials.

To investigate the doping in ncSi with high resistivity, we proposed an inverted MOS structure for CV measurements. Numerical CV modelling is developed to quantify the electrical properties such as doping concentration, doping type and interface trap density distribution. We investigated highly resistive boron doped ncSi films, which unexpectedly show a high doping concentration. The saturation of doping and the low doping efficiency, less than 5%, are observed and discussed. The corresponding low effective mobility is attributed to a strong scattering of excess impurities and defects.

Lastly, as a means to improve the electrical quality of these films, we demonstrated that a pulsed KrF excimer laser ( $\lambda$ =248 nm,  $\tau$ =22 ns) can be used as a post-furnace annealing method to greatly increase the electrically active doping concentration in ncSi, which potentially can reduce the extremely high impurity density currently used for doping ncSi. We propose that the increase in free carrier concentration after the laser treatment is the result of interstitial P/B dopants activation, which is initially inside the ncSi. Evidence of mobility-limited carrier transport and degenerate doping in the ncSi are measured with temperature-dependent conductivity, which further reveal the carrier-conduction mechanism in doped ncSi.

#### Declaration relating to disposition of project thesis/dissertation

I hereby grant to the University of New South Wales or its agents the right to archive and to make available my thesis or dissertation in whole or in part in the University libraries in all forms of media, now or here after known, subject to the provisions of the Copyright Act 1968. I retain all property rights, such as patent rights. I also retain the right to use in future works (such as articles or books) all or part of this thesis or dissertation.

I also authorise University Microfilms to use the 350 word abstract of my thesis in Dissertation Abstracts International (this is applicable to doctoral theses only).

Signature

Witness

Date

The University recognises that there may be exceptional circumstances requiring restrictions on copying or conditions on use. Requests for restriction for a period of up to 2 years must be made in writing. Requests for a longer period of restriction may be considered in exceptional circumstances and require the approval of the Dean of Graduate Research.

FOR OFFICE USE ONLY

Date of completion of requirements for Award:

#### **ORIGINALITY STATEMENT**

'I hereby declare that this submission is my own work and to the best of my knowledge it contains no materials previously published or written by another person, or substantial proportions of material which have been accepted for the award of any other degree or diploma at UNSW or any other educational institution, except where due acknowledgement is made in the thesis. Any contribution made to the research by others, with whom I have worked at UNSW or elsewhere, is explicitly acknowledged in the thesis. I also declare that the intellectual content of this thesis is the product of my own work, except to the extent that assistance from others in the project's design and conception or in style, presentation and linguistic expression is acknowledged.'

Signed

.....

Date

.....

#### **COPYRIGHT STATEMENT**

'I hereby grant the University of New South Wales or its agents the right to archive and to make available my thesis or dissertation in whole or part in the University libraries in all forms of media, now or here after known, subject to the provisions of the Copyright Act 1968. I retain all proprietary rights, such as patent rights. I also retain the right to use in future works (such as articles or books) all or part of this thesis or dissertation.

I also authorise University Microfilms to use the 350 word abstract of my thesis in Dissertation Abstract International (this is applicable to doctoral theses only).

I have either used no substantial portions of copyright material in my thesis or I have obtained permission to use copyright material; where permission has not been granted I have applied/will apply for a partial restriction of the digital copy of my thesis or dissertation.'

Signed

.....

Date

.....

#### AUTHENTICITY STATEMENT

'I certify that the Library deposit digital copy is a direct equivalent of the final officially approved version of my thesis. No emendation of content has occurred and if there are any minor variations in formatting, they are the result of the conversion to digital format.'

Signed

.....

Date

.....

## Abstract

This thesis presents insights into the electrical properties of doped silicon nanocrystals (ncSi) for 3<sup>rd</sup> generation photovoltaic solar cells. While investigating doping of PECVD ncSi-based PV devices (Chapter 3), it has become clear that commonly used techniques to dope and characterise these ncSi films are not effective. In view of this, specially designed structures for Capacitance-Voltage (CV) measurements and pulsed laser annealing techniques have been developed to characterise the doping effects and improve doping efficiency, respectively. Two first-author journal papers have been published based on the work presented in Chapter 4 and Chapter 5 of this thesis. Chapter 4 presents the research about CV measurements and evaluations of electrically active boron doping concentrations in ncSi. The work about improved dopants (Boron and Phosphorus) activation in ncSi by pulsed KrF laser is mainly included in Chapter 5. The characterization and fabrication techniques also presented in this thesis have assisted other journal publications on the research of doped ncSi material, ncSi-based photovoltaic devices and renewable energy applications.

The two most important contributions of this thesis are:

• The demonstration of an inverted MOS structure to measure doping using CV measurements and

• The improvement of the conductivity of ncSi films using a pulsed KrF excimer laser after the crystal growth.

This thesis starts with the investigation of plasma enhanced chemical vapour deposition (PECVD) for fabricating silicon nanocrystals along with boron (B) and phosphorus (P) doping. The material properties of non-stoichiometric silicon oxide before and after annealing and the B/P doped ncSi were investigated. After the demonstration of ncSi preparation and doping by PECVD, ncSi-based photovoltaic devices were eventually fabricated and analysed. The devices showed diode I-V characteristics and an open-circuit voltage of 230 mV was achieved. However, the parameters extracted from electrical measurements indicated severe limitations due to low carrier transport and strong non-radiative recombination. These limiting factors can be attributed to the ineffective doping in ncSi, which is a general problem for nanostructured semiconductor materials.

To investigate the doping in ncSi with high resistivity, we have proposed an inverted MOS structure for CV measurements. Numerical CV modelling was developed to quantify the electrical properties such as doping concentration, doping type and interface trap density distribution. We investigated highly resistive boron doped ncSi films, which unexpectedly showed a high doping concentration. The saturation of

doping and the low doping efficiency, less than 5%, were observed and discussed. The corresponding low effective mobility can be attributed to a strong scattering of excess impurities and defects.

Lastly, as a means to improve the electrical quality of these films, we demonstrated that a pulsed KrF excimer laser ( $\lambda$ =248 nm,  $\tau$ =22 ns) could be used as a post-furnace annealing method to greatly increase the electrically active doping concentration in ncSi. This technique potentially can reduce the extremely high impurity density currently used for doping ncSi. We propose that the increase in free carrier concentration after the laser treatment is the result of interstitial P/B dopants activation, which is initially inside the ncSi. Evidence of mobility-limited carrier transport and degenerate doping in the ncSi were measured with temperature-dependent conductivity, which further revealed the carrier-conduction mechanism in doped ncSi.

# **Unique Contributions**

The most significant contributions and novelties in this thesis are highlighted as below:

- The plasma enhanced chemical vapour deposition process details for silicon nanocrystal synthesis, doping and device fabrication, including the characterizations on structural, chemical and electrical properties.
- Demonstration and performance analysis of silicon nanocrystal based photovoltaic diode device on quartz substrate by PECVD.
- First demonstration of inverted MOS structure application compatible with capacitance voltage measurement to extract electrically active doping concentration in boron doped silicon nanocrystals with high resistivity.
- First demonstration of pulsed KrF laser annealing to active B/P dopants in silicon nanocrystals, including detailed structural and electrical characterizations.

## Acknowledgements

I would like to express my deepest gratitude to all the people who have contributed to this thesis by experimental support, discussions, inspirations and motivations.

First of all, I would like to thank Dr. Ivan Perez Wurfl for his continuous motivations in realizing my ideas, open-handed trainings and in-depth discussions on my experiments, also his great patience. I would also like to thank Prof. Gavin Conibeer for his leadership of Third Generation Group to provide such a well-equipped, open-minded and friendly research environment. With their supports, my research and study during my PhD period has always been fascinating and fruitful. Special thanks should go to my dear group colleagues Dr. Lingfeng Wu, Dr, Binesh Puthen-Veettil, Dr. Ziyun Lin, Dr. Terry Chien-Jen Yang, Keita Nomoto and Dr. Xuguang Jia for their extensive experimental supports, the excellent teamwork and the numerous discussions. To be more specific on the experimental supports from my colleagues, Dr. Lingfeng, Dr. Terry Chien-Jen Yang and Dr. Xuguang Jia gave me great help on the RF-sputtering training and sample preparation, Dr. Binesh Puthen-Veettil helped on many photoluminescence (PL) characterization and discussions, the excellent transmission electron microscopy (TEM) and the atomic probe tomography (APT) images in Chapter 5 were from Keita Nomoto, and Dr. Ziyun Lin did the atomic force microscopy (AFM) experiments for surface morphology investigation. Their encouragement and friendship is one of the greatest achievements I have obtained from my PhD study.

Secondly, I would like to thank many people in laboratory development and operation team (LDOT) in the Photovoltaic School for their great efforts on equipment trainings and maintenances. They are Dr. Patrick Campell, Tom Puzzer, Mark Griffin, Mark Silver, Alen Yee, Kian Chin, Nicholas Shaw and Bernhard Vogl. I also express my gratitude to Dr. Yu Wang and Dr. Bill Gong from the Solid State and Elemental Analysis Unit (SSEAU) UNSW for the XRD training and XPS measurements, respectively. Dr. Anne Rich from the Spectroscopy Laboratory UNSW for the Raman spectroscopy training and equipment preparation.

I also thank the following collaborators for their contributions:

- Dr.Brian Simonds from National Institute of Standards and Technology for his generous support and insightful discussions. His inspirations and research attitudes have changed my mind about doing research.
- Dr. Birger Berghoff, Dr. Stephan Suckow and Dr. Noel Wilck from the Institut für Halbleitertechnik, RWTH Aachen University for their expertise of PECVD deposition technology.

Furthermore, I give my particular thanks Dr. Dirk König, Dr. Shujuan Huang, Dr. Rob Patterson, Dr.Yu Feng, Dr.Jialiang Huang and Dr.Wei Li for spending their precious time on sharing their expertise, knowledge and insightful discussions on characterization techniques and theory.

I gratefully acknowledge the Australian Federal Government for the provision of the Australian Postgraduate Award (APA) scholarship to fund my PhD study in UNSW.

Finally, I thank my parents and my wife Huichun Wang for their enduring understanding, boundless love, belief and support without reservation.

# **Publication List**

#### **Peer-Reviewed Journal Articles:**

**J1. Zhang, T.,** Simonds, B., Nomoto, K., Puthen Veettil, B., Lin, Z., Perez Wurfl, I., and Conibeer, G.: 'Pulsed KrF excimer laser dopant activation in nanocrystal silicon in a silicon dioxide matrix', Applied Physics Letters, 2016, 108, (8), pp. 083103

**J2. Zhang, T.,** Puthen-Veettil, B., Wu, L., Jia, X., Lin, Z., Yang, T.C.-J., Conibeer, G., and Perez-Wurfl, I.: '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, 2015, 118, (15), pp. 154305

**J3.** Lingfeng Wu, **Tian Zhang**, Ziyun Lin, Xuguang Jia, Binesh Puthen-Veettil, Terry Chien-Jen Yang, Hongze Xia, Gavin Conibeer, Ivan Perez-Wurfl, 'Silicon nanocrystal photovoltaic device fabricated via photolithography and its current–voltage temperature dependence', Solar Energy Materials and Solar Cells, 2014, 128, pp.435-440

**J4.** Felipe Crisostomoa, Robert A. Taylor, **Tian Zhang**, Ivan Perez-Wurfl, Gary Rosengarten, Vernie Everett, Evatt R. Hawkes, 'Experimental testing of SiNx/SiO2 thin film filters for a concentrating solar hybrid PV/T collector', Renewable Energy, 2014, vol 72, pp.79-87

**J5.** Wu, L., Puthen-Veettil, B., Nomoto, K., Hao, X., Jia, X., Lin, Z., Yang, T.C., **Zhang, T.,** Gutsch, S., Conibeer, G., and Perez-Wurfl, I.: 'Temperature dependent electroluminescence from all-Sinanocrystal p-i-n diodes grown on dielectric substrates', Journal of Applied Physics, 2016, 119, (6), pp. 063102

J6. Liu, X., Huang, Y., Yun, J., Wen, X., Lu, Z., Zhang, T., Cui, H., Li, W., Lee, C.-Y., Xu, S., Hao, X., and Conibeer, G.: 'Characterization of a Cu2ZnSnS4 solar cell fabricated by sulfurization of metallic precursor Mo/Zn/Cu/Sn', physica status solidi (a), 2015, 212, (9), pp. 2074-2079

**J7.** Lin, Z., Wu, L., Jia, X., **Zhang, T**., Puthen-Veettil, B., Yang, T.C.-J., Conibeer, G., and Perez-Wurfl, I.: '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, 2015, 118, (4), pp. 045303

**J8.** Puthen Veettil, B., Wu, L., Jia, X., Lin, Z., **Zhang, T.,** Yang, T., Johnson, C., McCamey, D., Conibeer, G., and Perez-Würfl, I.: 'Passivation effects in B doped self-assembled Si nanocrystals', Applied Physics Letters, 2014, 105, (22), pp. 222108

**J9.** Yang, T.C.-J., Kauffmann, Y., Wu, L., Lin, Z., Jia, X., Puthen-Veettil, B., **Zhang, T.,** Conibeer, G., Perez-Wurfl, I., and Rothschild, A., 'In-situ high resolution transmission electron microscopy observation of silicon nanocrystal nucleation in a SiO2 bilayered matrix', Applied Physics Letters, 2014, 105, 053116 DOI: 10.10631/1.4892658

#### **Conference Proceedings:**

**C1.** Brian J. Simonds, Anthony Teal, **Tian Zhang**, Josh Hadler, Zibo Zhou, Sergey Varlamov, Ivan Perez-Würfl, 'Dual-beam laser thermal processing of silicon photovoltaic materials', Proceedings of SPIE – Photonic West Laser, San Francisco, USA, February 2016

**C2. Tian Zhang**, Ivan Perez Wurfl, Binesh Puthen Veettil, Lingfeng Wu, Xuguang Jia, Ziyun Lin, Chien Jen Yang, Gavin Conibeer, 'Capacitance-Voltage Characterization of In-situ Boron Doped Silicon Quantum Dot in Silicon Dioxide', Proceedings of 40th IEEE Photovoltaic Specialists Conference, Denver, USA, June 2014

# Contents

Abstract	i
Unique Contributions	iv
Acknowledgements	V
Publication List	vii

Contents	9
List of Figures	

Chap	ter 1 Introduction	18
1.1.	Basic principles of quantum-confined silicon nanocrystals	18
1.2.	The "all silicon" tandem solar cells	26
1.3.	Challenges of doping silicon nanocrystals	31
1.4.	Carrier transport in intrinsic and doped ncSi	35
1.5.	Thesis aims and outlines	40

Chap	ter 2	Experimental Details	44
2.1.	Fabrica	ation of Silicon Nanocrystals	44
	2.1.1.	Superlattice approach for size-controlled silicon nanocrystals	45
	2.1.2.	Radio-Frequency magnetron co-sputtering deposition	47
	2.1.3.	Plasma enhanced chemical vapour deposition (PECVD)	49
	2.1.4.	Thermal annealing process	52
	2.1.5.	Pulsed laser annealing process	53
2.2.	Charac	eterization Methods	55
	2.2.1.	Fourier Transform Infrared Spectroscopy (FTIR)	55
	2.2.2.	Photoluminescence	. 57
	2.2.3.	X-Ray Diffraction	. 58
	2.2.4.	Raman spectroscopy	. 60
	2.2.5.	Electrical characterization	. 63
	2.2.6.	Hall effect measurement	. 64
	2.2.7.	Atom probe tomography	. 66
2.3.	Conclu	ision	68

Chap	ter 3 PECVD Silicon Nanocrystal Fabrication and Tentative
ncSi I	Based Photovoltaic Device
3.1.	Introduction
3.2.	Basic stoichiometry control and chemical characterization of as-deposited SRO
3.3.	Structural and chemical properties of the annealed SRO

	3.3.2.	Nitrogen and hydrogen in annealed SRO	82
	3.3.3.	Rapid Thermal Annealing for Crystallization	87
3.4.	Boron	and Phosphorus Doping in Silicon Nanocrystals	90
	3.4.1.	In-Situ Doping	91
	3.4.2.	Diffusion Doping Method	98
3.5.	Tentat	ive ncSi-Based Photovoltaic Devices by PECVD	101
	3.5.1.	Device Fabrication Process	101
	3.5.2.	Measured I-V Characteristics	104
	3.5.3.	Further Device Process Development	111
3.6.	Conclu	ision	115

## 

4.1.	Introdu	uction	118
4.2.	The In	verted MOS Devices	121
	4.2.1.	Sample preparation	
	4.2.2.	Advantages of The Inverted MOS Structure	
4.3.	Structu	aral characterization using XRD	
4.4.	Photol	uminescence characterization	
4.5.	CV Me	easurement Results and Discussions	129
	4.5.1.	CV characteristics of boron doped ncSi MOS	
	4.5.2.	CV frequency dispersion	134
	4.5.3.	Capacitance Voltage Modelling	
4.6.	Electri	cal Properties of Boron Doped Si Nanocrystals	141

4.7. Conclusion	146
-----------------	-----

## 

5.1.	Introduction	150
5.2.	Sample Preparation and Pulsed Laser Annealing	153
5.3.	Structural Characterization after Pulsed Laser Annealing	157
5.4.	Identification of Dopant Activation by PLA	162
5.5.	Discussion on ncSi Doping and Carrier Conduction	166
5.6.	Mechanisms of Dopant Activation by PLA	170
5.7.	Conclusion	172

Chapter 6		Further Discussions, Conclusions and Future		
•••••			•••••	174
6.1.	Further	Discussions		174
	6.1.1.	Importance of carrier lifetime	•••••••••••	175
	6.1.2.	Importance of carrier mobility	•••••••••••	177
	6.1.3.	Summary of factors limiting PV performance		179
6.2.	Conclu	sions		179
6.3.	Future	Work		184
REFI	ERENC	EES	•••••	188

# **List of Figures**

Figure 1.1: The schematic quantum confinement in 1-D quantum well
Figure 1.2: Joint density of states of bulk semiconductor and quantum-confined semiconductor22
Figure 1.3: Comparison of calculated bandgap by EMA and the PL emission peaks in the function of silicon nanocrystal size
Figure 1.4: The band offset of crystal silicon confined in high bandgap dielectric material (SiO2, Si3N4 and SiC)
Figure 1.5: Loss mechanisms in a standard p-n junction solar cell
Figure 1.6: The all-silicon solar cell
Figure 1.7: The p-i-n ncSi-based solar cell on quartz substrate
Figure 1.8: The APT proxigram of the phosphorus distribution across the ncSi interface32
Figure 1.9: Schematic representation of donor in bulk silicon (a) and nanocrystal silicon (b)34
Figure 1.10: HRTEM images of three Si phase contents: isolated, touching and percolation silicon nanocrystals
<b>Figure 2.1:</b> Schematic of as-deposited a-SiOx/SiO2 superlattice film and structure of Si nanocrystals embedded in SiO <sub>2</sub>
Figure 2.2: Schematic diagram of the RF magnetron sputtering system used for sample fabrication.
<b>Figure 2.3:</b> (a) The plasma enhance chemical vapour deposition system used for ncSi fabrication. (b)
The schematic diagram of the capacitively coupled RF plasma deposition system

Figure 2.4: The XRR result for a superlattice structure consisting of 20 bilayers (4 nr	n SRO/2 nm
SiO2). The bilayer thickness evaluated from the Bragg peaks is 5.7 nm.	
<b>Figure 2.5:</b> The principle of Hall Effect for carrier concentration evaluation and the V contact for resistivity and thin film Hall measurement.	an-der-Pauw 66
Figure 3.1: Refractive index of SRO fabricated at various SiH <sub>4</sub> % level	72
Figure 3.2: XPS N1s and Si2p level results	75
Figure 3.3: FTIR spectra of as-deposited SRO fabricated by PECVD	77
Figure 3.4: Si-H stretching mode peak shifts with SiH <sub>4</sub> :N <sub>2</sub> O ratio	79
<b>Figure 3.5:</b> The X-ray diffraction results of silicon rich oxide by PECVD after 1100 annealing in a N <sub>2</sub> ambient for 1 hour	) °C furnace 82
Figure 3.6: FTIR spectra of PECVD SRO before and after 1100 °C furnace annealing.	
<b>Figure 3.7:</b> The optical refractive index (a) and absorption coefficient (b). The increase coefficients after furnace annealing (dashed lines) and RTP (dotted lines) are clearly ind arrows shown in (b).	d absorption icated by the 85
Figure 3.8: Raman spectroscopy results of PECVD SRO materials annealed by furnace and RTP (b)	annealing (a) 88
<b>Figure 3.9:</b> FTIR results of B and P doped SRO by PECVD. No chemical composition to doping can be observed.	n change due
Figure 3.10: Circular-TLM structure pattern	93
Figure 3.11: Detailed TLM results of phosphorus doped SRO after 1100°C annealing	94
Figure 3.12: Detailed TLM results of boron doped SRO after 1100°C annealing	95
Figure 3.13: The resistivity of B and P doped SRO after annealing as the function of Si	H4%95
Figure 3.14: The sample structures for the diffusion doping method	99
Figure 3.15: Sheet resistance of B/P doped ncSi by the diffusion doping method	100
Figure 3.16: The PECVD ncSi based p-i-n diode device structure.	101

Figure 3.17: Dark IV and Light IV results of ncSi based photovoltaic devices fabricated by PECVD   deposition   106
Figure 3.18: The typical single junction solar cell equivalent circuit107
<b>Figure 3.19:</b> The series resistance effect on the I-V characteristics of PIN1_0i device. The red dot line is the IV results after series resistance removal
Figure 3.21: The cross-section SEM image of the RIE etched annealed ncSi thin film112
Figure 3.22: Lift-off process using double layer PR to avoid reactive ion etching
Figure 4.1: (a) The lateral MOS device. (b) The inverted MOS device121
<b>Figure 4.2:</b> The photolithography mask for Al metallization patterning. The right pattern is the circular TLM next to the MOS devices on the left
Figure 4.3: The capacitance is only linearly proportional to the gate area, which indicates that there is no edge effect in the inverted MOS device. The frequency and the gate bias voltage ( $V_b$ ) also do not change the linear relationship. FGA means forming gas annealing
<b>Figure 4.4:</b> (a) The I-V results by TLM measurement showing the contact is ohmic. (b) The TLM plot (resistance vs. ln(Rout/Rin)) for the calculation of sheet resistivity and the contact resistance. The sample shown here is boron doped ncSi with 5W sputtering power
Figure 4.5: The GIXRD results show the characteristic Si XRD peaks, which confirm the existence of ncSi
<b>Figure 4.6:</b> (a) PL spectra measured from the intrinsic ncSi and boron doped ncSi. (b) The normalized PL results. The normalized PL spectra of ncSi doped with boron power 10W and 15W are identical.
Figure 4.7: Equivalent circuit of MOS in accumulation and inversion conditions
<b>Figure 4.8:</b> CV results of boron doped ncSi with various doping power (a) B5W, (b) B10W, (c) B15W. The CV curves shift down with higher frequency. The corrected CV results (d, e, f) without frequency dispersion.
<b>Figure 4.9:</b> (a) The CV results of boron power 5W before forming gas annealing. (b) The corrected CV results

Figure 4.10: The schematic of displaced charges causing the frequency dispersion
Figure 4.11: Fitting results of 1MHz high frequency CV curves for various boron densities141
Figure 4.12: Interface traps distribution results. D <sub>ita</sub> means the acceptor-like traps density and D <sub>itd</sub> means the donor-like traps density
Figure 5.1: (a) The cross section TEM of p-i-n ncSi solar cell. (b) The proxigram results of B/P doped ncSi interface
<b>Figure 5.2:</b> (a) The cross section TEM Plasmon image of the P doped ncSi after furnace annealing (no pulsed laser). The white regions are Si clusters in various sizes. (b) The HRTEM image directly showing the existence of interconnected silicon nanocrystals (the lattice fringes)
<b>Figure 5.3:</b> Atomic probe tomography results of the (a) 3D structural details of ncSi, (b) Identification of isolated ncSi, (c) identification of connected ncSi, and (d) the proxigram of the boron distribution across the ncSi interface
Figure 5.4: (a) the laser beam uniformity tested by CCD sensor array. (b) The schematic pulsed laser annealing system
<b>Figure 5.5:</b> The AFM results of boron doped ncSi after 202± 5 mJ/cm <sup>2</sup> annealing. The average roughness is about 1.29nm
Figure 5.6: The AFM results of phosphorus doped ncSi after 202± 5 mJ/cm <sup>2</sup> annealing. The average roughness is about 0.9nm. 158
Figure 5.7: The AFM results of phosphorus doped ncSi after only furnace annealing. The average roughness is about 2.36nm. 159
Figure 5.8: Experimental Raman spectra of phosphorus (a) and boron (b) doped ncSi161
Figure 5.9: The pulsed laser annealing effects on (a) free-carrier concentration, (b) mobility and (c) conductivity

**Figure 5.10:** (a) Temperature-dependent Hall measurement results of phosphorus doping concentration over the temperature range from 150 K to 350 K. (b) A T-1/4 fitting plot of conductivity of phosphorus-doped ncSi annealed by different laser fluences from 0 mJ/cm2 to 202 mJ/cm2. .. 167

Figure 5.11: Photoluminescence (PL) results of highly phosphorus (a	) and boron (b) doped ncSi by
PLA process, which show red-shift by higher laser fluence. (c) The PL	intensity as a function of laser
power density	

## **Chapter 1**

# Introduction

**Overview:** The quantum confinement mechanism in low dimensional silicon crystals and the theoretical illustration of its application for 3<sup>rd</sup> generation photovoltaic devices are summarized. The quantum size-effect model, solar cell energy loss mechanisms, 3<sup>rd</sup> generation photovoltaic concepts and ncSi based photovoltaic devices have been reviewed. Additionally, this chapter has also emphasised on the current research progresses on ncSi doping and challenges, followed by the summary of carrier transport mechanisms in intrinsic and doped ncSi.

### 1.1. Basic principles of quantum-confined silicon nanocrystals

Since the discovery of light emission from porous silicon in 1990 by Canham and Cullis [1, 2], it has been realised that the optical and electrical properties of crystalline silicon can be further modified by reducing the crystal size in the order of nanometres.

In the following decades, various forms of nanostructured silicon with precisely controlled structures, such as nanosheets, nanowires and nanoparticles, have been investigated. The observed strong correlation between the nanocrystal structure (size and density) and the optical emission energy and absorption indicate the possibility of modifying the fundamental Si energy bandgap, which is attributed to the quantum confinement effect. [3]



Figure 1.1: The schematic quantum confinement in 1-D quantum well

The basic physical phenomenon of quantum confinement arises as a result of the quantization effect in the density of electronic states. This quantization effect can be illustrated in the simplified one-dimensional quantum well model with one-directional confinement as shown in Figure 1.1. The carrier energies and the wave functions can

be solved using *Schrödinger's equation* with an effective mass approximation (EMA). The energy of the confined electron in the quantum well with confining size  $\alpha$  and infinite barrier height can be written as:

$$\Delta E_x = \frac{\hbar^2 k^2}{2m^*} = \frac{\hbar^2 n^2 \pi^2}{2m^* a^2} \tag{1.1}$$

where k is the wavevector,  $\hbar = h/2\pi$  is the reduced Planck constant and m\* is the effective mass of electrons or hole carriers. The relation k. $\alpha = n.\pi$  is derived from the boundary condition of total confinement by the infinite barrier height.

From equation 1.1, the collapse of the continuous energy band into discrete energy levels (n=1,2,3....) can be clearly identified. As shown in Figure 1.1, the first allowed energy level, corresponding to n=1, is higher than the lowest conduction band edge. Therefore, the effective energy bandgap of a quantum-confined semiconductor, which should be more precisely defined as the HOMO-LUMO gap (highest occupied molecular orbital and lowest unoccupied molecular orbital), becomes larger than the bandgap of the corresponding bulk semiconductor. The increased energy bandgap caused by quantum confinement is clearly dependent on confinement size  $\alpha$ , which is known as 'quantum-size effect'. [4, 5]

Theoretically, this quantum-size effect becomes most important when the confinement size is similar or smaller than the bulk semiconductor Bohr exciton

radius. The Bohr radius can be defined as the minimum distance between an electronhole pair. For silicon nanocrystals, the Bohr exciton radius is about 5 nm, indicating that silicon nanocrystals with a size of 5 nm or less will present strong quantum confinement. [1] Silicon nanocrystals about 2–4 times larger than Bohr radius will show weaker quantum confinement.

The 2-D quantum well model can be further extended to a 3-D model to illustrate the more practical cases of quantum dots, quantum wires and quantum wells with different numbers of confinement directions. Then the Schrödinger equations will contain x, y and z components. The idealised solutions of energy are in the forms:

Quantum dot: 
$$E_{n,m,l} = \frac{\pi^2 \hbar^2}{2m^*} \left( \frac{n^2}{L_\chi^2} + \frac{m^2}{L_y^2} + \frac{l^2}{L_z^2} \right)$$
 (1.2)

Quantum wire: 
$$E_{n,m}(k_z) = \frac{\pi^2 \hbar^2}{2m^*} \left( \frac{n^2}{L_x^2} + \frac{m^2}{L_y^2} \right) + \frac{\hbar^2 k_z^2}{2m^*}$$
(1.3)

Quantum well: 
$$E_n(k_y k_z) = \frac{\pi^2 \hbar^2 n^2}{2m^* L_x^2} + \frac{\hbar^2 (k_y^2 + k_z^2)}{2m^*}$$
 (1.4)

where n, m, l = 1, 2, 3 ... are the confinement numbers, and  $L_x$ ,  $L_y$  and  $L_z$  are the confinement size. For a simple comparison, by considering n=m=l,  $L_x=L_y=L_z=a$ , and k=0, it is conceivable that higher energy levels can be achieved in higher confinement dimensions (quantum dot > quantum wire > quantum well). To be more specific, this means the diameter requirement of the quantum dot will be  $\sqrt{3}$  times less than the quantum well for the same level of quantum confinement. [6]



Figure 1.2: Joint density of states of bulk semiconductor and quantum-confined semiconductor [7]

The quantization of energy levels results in the quantization of density of electronic states, which can be identified in the calculated joint density of states, as shown in Figure 1.2. Compared with bulk semiconductors, quantum-confined semiconductors clearly show larger bandgap, quantized density of states and stronger selective transition (absorption/emission) at higher confinement dimensions. These effects have been experimentally observed as the shift in absorption onset and photoluminescence emission by reducing the diameter of silicon nanocrystals.

By identifying the tunable energy bandgap as the most striking property of nanocrystals, a theoretical energy bandgap calculation for semiconductor nanocrystals was reported by Brus et al. based on "effective mass approximation" (EMA). [8] A spherical volume of the crystallite with a confined exciton was considered [9]:

$$E_g = E_{bulk} + \frac{h^2}{8R^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.786e^2}{4\pi\varepsilon_0\varepsilon_r R}$$
(1.5)

, where  $E_g$  is the bandgap,  $E_{bulk}$  is the bandgap of bulk semiconductor, R is the radius of nanoparticle,  $m_e^*$ ,  $m_h^*$  are the effective mass of excited electron and hole,  $\varepsilon_0$ , and  $\varepsilon_r$ are the vacuum and relative permittivity. The second term having the R<sup>-2</sup> dependence represents the quantum confinement by the infinite barrier potential. The third term showing an R<sup>-1</sup> dependence stands for the columbic interaction, which can be neglected if the high dielectric constant of semiconductor materials is considered. Specifically, for silicon nanocrystals, Conibeer et al. quantified the effective bandgap by using  $m_e^* = 0.27 m_0$  and  $m_h^* = 0.59 m_0$ :

$$E = E_{Si} + \Delta E_e + \Delta E_h = E_{Si} + \frac{4.181}{R^2} + \frac{1.93}{R^2}^1$$
(1.6)

, where R is the crystal size (nm) and Esi is 1.12eV. [6]

In general, the trends in photoluminescence emission spectral shift and various silicon nanocrystal sizes have corresponded well with the theoretical prediction, which offers a possibility for bandgap engineering by controlling the size of the silicon nanocrystals. [10] However, it must be noted that the experimental values in the shift of the PL peak are consistently lower than the theoretical predictions. The inaccuracy in the prediction increases as the size of the nanocrystals is reduced (Figure 1.3).



**Figure 1.3:** Comparison of calculated bandgap by EMA and the PL emission peaks [11-14] in the function of silicon nanocrystal size [6]



**Figure 1.4:** The band offset of crystal silicon confined in high bandgap dielectric material (SiO2, Si3N4 and SiC) [6]

This reduced confinement energy can be partly explained by the actual finite barrier height. The solid-state quantum-confined silicon nanocrystals are generally formed in a large bandgap dielectric matrix (SiO<sub>2</sub>~9 eV, Si<sub>3</sub>N<sub>4</sub>~6 eV and SiC ~2.5 eV) by phase separation and silicon cluttering in non-stoichiometric compounds after high-temperature annealing. As shown in Figure 1.4, the ideal highest barrier height can only be achieved from SiO<sub>2</sub> for 3.2 eV (electron) and 4.7 eV (hole). The energy of the confined energy level will be diminished as given by:

$$\Delta E_n \approx 3 \cdot \frac{\pi^2 \hbar^2}{8m^* R^2} \cdot n^2 / \left[ 1 + \frac{\hbar}{2R/\sqrt{2m^* V_0}} \right]^2$$
(1.7)

where  $V_o$  is the corresponding barrier height, R is the crystal size and m<sup>\*</sup> is the effective mass. [15]

Additionally, the confinement energy also depends strongly on the non-ideal confinement factors that occur in practice, such as the presence of complex nanoparticle surface states, the narrow spacing between nanocrystals and the defect states in the barrier matrix.

Besides the ability to modify the energy bandgap, quantum confinement in nanocrystal silicon also exhibits dramatic enhancements in the optical transitions which can be observed as an improved photoluminescence. In bulk silicon, the absorption and photoemission is limited by momentum conservation. Because of the indirect bandgap in bulk silicon, phonons are required to assist radiative transitions. However, in silicon nanocrystals, the electron-hole wavefunctions are confined in a box-like potential. Following Heisenberg's uncertainty principle, as the position and energy of excitons become more certain in the nanocrystal, the momentum will be less well defined. Therefore, a series of transitions requiring different momentums in the bulk silicon will be compressed by quantum confinement into a single and intense transition, making silicon nanocrystals behave like a "direct bandgap" semiconductor. The unique properties arising from quantum confinement, make silicon nanocrystal attractive for applications in photoelectronic and photovoltaic devices.

### 1.2. The "all silicon" tandem solar cells

A solar cell is a large area semiconductor photoelectronic device, which can directly convert electromagnetic radiation energy into electrical energy via the photovoltaic effect. For this purpose, p-n junctions or build-in electric fields are fabricated in semiconductor materials to enhance the separation of electron-hole pairs generated by the absorbed light (photons), so as to generate an electrical current. These type of electronic devices waste a large portion of sunlight power due to generated heat and light transparency. In silicon solar cell, the amounts of losses are 23% and 33% of the incoming solar energies, respectively. [16] The loss mechanisms in such a structure can be illustrated by analysing a single bandgap p-n junction diode (Figure 1.5).



**Figure 1.5:** Loss mechanisms in a standard p-n junction solar cell [6]: (1) Non-absorption of hv<br/>bandgap photons. (2) Lattice thermalization loss (>50%). (3) Junction loss. (4) Contact voltage losses. (5) Recombination loss (radiative recombination).

The two most important power-loss mechanisms are the inability to absorb photons with energy less than the semiconductor bandgap (Figure 1.5 (1)), and the thermalization of the generated carriers by photons with energy exceeding the bandgap (Figure 1.5 (2)). These two factors have already theoretically limited the conversion efficiency to 31% for a general single bandgap solar cell through a detailed balance calculation, which is known as the "Shockley-Queisser limit". [16] The other losses due to the voltage drop across internal resistances and contacts (Figure 1.5 (3) and (4)) the non-radiative minority carrier recombination (Figure 1.5 (5)) will further

reduce conversion efficiency. These losses however are, relatively small compared with loss mechanisms (1) and (2). Therefore, it is important to concentrate improving light absorption and reducing thermalization.

Three approaches have been proposed to overcome the Shockley-Queisser limit:

- a) Multi-junctions by using semiconductors with different bandgaps to increase the light absorption and reduce the thermalization
- b) Reduction of thermalization loss by capturing hot carriers
- c) Excitation by multiple low-energy photons or multiple carrier generation by one high-energy photon.

Multi-junction solar-cells offer the only effective method to achieve efficiencies over the 33.7% Shockley-Queisser limit. An astonishing 38.8% from a five-junction solar cell based on III/V group semiconductor materials has been reported under AM1.5 illumination. [17] However, these solar cells are extremely expensive to fabricate, and are nowadays only used for military or space applications. Additionally, the III/V group semiconductor materials are not earth-abundant elements for commercial applications.

Quantum-confined silicon nanocrystals embedded in  $SiO_2$  with a tunable and pseudodirect bandgap, as described in the previous section, also fulfil the criteria for the fabrication of tandem solar cells. Moreover, silicon and its dielectric compounds are readily available materials, which can be fabricated with thin film techniques compatible with large-scale manufacture. In this technology, the "all-silicon" tandem cell would be realised by using a traditional silicon solar cell as the bottom cell and a silicon nanocrystal cell with higher bandgap as the top cell in a stack structure. Theoretically, the conversion efficiency increases to 42.5% for a 2-cell tandem structure using 1.7 eV-1.8 eV optimal bandgap of the top cell, to 47.5% for a 3-cell tandem cell structure using 1.5 eV and 2.0 eV optimal bandgaps of the middle and top cell, respectively. The possible structure of a 3-cell tandem cell is illustrated in Figure 1.6.



**Figure 1.6:** The all-silicon solar cell consists of bulk Si solar cell as bottom cell, 1.5eV silicon nanocrystal middle cell and 2.0eV silicon nanocrystal top cell. [18] The solar spectrum will be split and absorbed by different cells to achieve high-energy conversion efficiency.



Figure 1.7: The p-i-n ncSi-based solar cell on quartz substrate [19]

Despite the apparent simplicity of the all-silicon tandem cell, the main barrier for fabricating such devices is the lack of silicon nanocrystals with the desired electrical properties. An experimental demonstration of a single junction device based on ncSi materials was reported by Perez Wurfl et al. at UNSW. [19] In this work, a p-i-n structure diode was fabricated by sputtering alternating layers of 2 nm silicon dioxide (SiO<sub>2</sub>) and 4 nm silicon-rich oxide on quartz substrates with in-situ boron (B) and phosphorous (P) doping. The device structure is shown in Figure 1.7. Although the best ncSi solar cell achieved an open-circuit voltage of 490 mV, the short-circuit current measured is only 0.02 mA/cm<sup>2</sup>, four orders of magnitude This photovoltaic performance is much lower than what is required for high-efficiency tandem solar cells. The extremely low short-circuit current can be attributed to the large sheet resistance. The low material lifetime can also contribute to the low open-circuit

voltage and low short-circuit current. Further improvements are required in the material properties and device architecture.

### 1.3. Challenges of doping silicon nanocrystals

As a p-n junction is the prerequisite for functional ncSi-based photovoltaic devices, it is important to investigate the doping of silicon nanocrystals. Both electronic p- and n-type doping in ncSi have been achieved with boron and phosphorus, respectively. It has been shown that the conductivity of ncSi can be improved by several orders of magnitude using these dopants. [20, 21] However, the doping of ncSi has shown quite distinct properties from the corresponding bulk silicon, such as the reduced carrier concentration due to low doping efficiency and the dependence of dopant incorporation on the surface morphology and size of the nanocrystals during growth.

Two fundamental challenges have been identified when doping ncSi: (a) the selfpurification mechanism during silicon nanocrystal growth; and (b) the increased dopant ionisation energy in quantum-confined silicon.


Figure 1.8: The APT proxigram of the phosphorus distribution across the ncSi interface [22]

Self-purification in silicon nanocrystals will make the dopants aggregate at the ncSi interface rather than stay inside the nanocrystal. This results in low doping efficiency [23] and large amounts of electrically inactive dopants and defects formed at the ncSi interface. [24] The effect has been experimentally confirmed by observation of the effective removal of dopants aggregated at the nanocrystal interface by etching ncSi surface oxide in hydrofluoric acid (HF). [25, 26] More direct evidence of P aggregation at the ncSi interface can be identified from phosphorus concentration peak at the ncSi interface by 3D atom probe tomography (APT), as shown in Figure 1.8.

Successful doping requires the incorporation of electrically active impurity atoms inside silicon nanocrystals by substitutionally occupying the silicon lattice sites. As the impurity atom size is usually different from the host lattice, the substitutional dopants inevitably cause local stress or strain in nanocrystals. Therefore, the doped ncSi can relive the stress or strain by expelling the impurity atoms to the ncSi surface. From a kinetic perspective, the heat treatment at high temperature enhances the diffusion of impurities, defects and dislocations to the nearby nanocrystal surface. [27] Moreover, this self-purification size effect can be further interpreted from an energetic perspective considering the substitutional dopant formation energy in ncSi increases as the nanocrystal size is reduced. From the theoretical calculation by Cantele et al. [28] and Xuan Luo et al. [29], the formation energy of substitutional boron and phosphorus dopants in relaxed bulk silicon are approximately 0.8eV and 0.2eV, respectively. However, the formation energy will increase to 1 eV-2 eV depending on the reduced size and the local constrained environment of ncSi. [30] Using firstprinciples total-energy calculations of the doped silicon nanocrystal with single phosphorous atom positioned from centre to surface, it has been identified that P at the surface of silicon nanocrystal is more energetically stable. [31]



Figure 1.9: Schematic representation of donor in bulk silicon (a) and nanocrystal silicon (b).

The increased ionization energy of dopants in ncSi depends on the higher energy states (larger bandgap) owing to the quantum confinement by the dielectric potential barriers. As shown in Figure 1.9 (b), the ionization energy is the difference between the first miniband and the donor state energy level, leading to localised wavefunctions and constrained electrons. Therefore, in the spatially isolated nanocrystals, the electrons or holes are highly localised at the donor or acceptor ions. Hence, the room temperature dopant ionization should be highly unlikely. In contrast, in bulk silicon (Figure 1.9 (a)), the shallow donor levels lead to the electrons being loosely bound to the donor ions and a delocalised electron wavefunction  $|\psi|^2$ . This effect in ncSi has been experimentally identified for low phosphorus doped isolated nanocrystals showing that the conductivity (which is also very low) is independent of the doping concentration, the conductivity shows a steep increase proportional to the doping concentration. [25] Hybrid density function theory (h-DFT) calculations of single phosphorus dopant in the ncSi/SiO<sub>2</sub> system also theoretically illustrate that the P

dopants should work as deep-level defects but still contributing to an improved conductivity and to photoluminescence (PL) quenching in doped ncSi. [32]

Owing to the low-doping efficiency caused by the self-purification mechanism and the high-dopant-ionization-energy, no effective doping in ncSi has been observed at low- or medium-doping density ( $<10^{+18}$  cm<sup>-3</sup>) or in small and isolated ncSi in SiO<sub>2</sub>. [23-25] The successful doping of ncSi is generally achieved by using very high atomic doping density in the range of 0.13 at.% to 5 at.% ( $\sim 10^{+19}$  to  $10^{+21}$  cm<sup>-3</sup>). [26, 33-35] This high level of dopant density will not only influence the silicon nanocrystal growth process in terms of shape and size, but the carrier transport mechanism can also be altered. Additionally, the unavoidable generated defects caused by the high density of impurities will deteriorate the material. Therefore, the improvement of doping efficiency in ncSi is of great research interest for the improvement of ncSibased photovoltaic device performance, which is also a general challenge for doping in semiconductor nanocrystal materials.

## 1.4. Carrier transport in intrinsic and doped ncSi

The carrier transport of ncSi embedded in  $SiO_2$  is much more complex than that of bulk silicon because of the inherent complexity in structural and chemical properties. It is conceivable that the way carriers transport across the high-potential barrier from the dielectric matrix and the crystal boundary mainly determines the carrier conduction.

For intrinsic ncSi embedded in a SiO<sub>2</sub> matrix, the carrier transport is commonly attributed to direct tunnelling because of the large band offset between Si and SiO<sub>2</sub> that would preclude any other path (assuming a perfect SiO<sub>2</sub> barrier) The tunnelling probability strongly depends on the barrier height and ncSi spacing (barrier width). From a consideration of transmission/reflection probability, the tunnelling probability (T<sub>e</sub>) through a square potential well can be expressed as:

$$T_e \approx 16 \exp\left\{-d\sqrt{\frac{8m^*}{\hbar^2}\Delta E}\right\}$$
 (1.8)

, where d is the barrier width,  $\Delta E$  is barrier height and m\* is the effective mass of carriers.



**Figure 1.10:** HRTEM images of three Si phase contents: isolated, touching and percolation silicon nanocrystals. The carrier transport is determined by the ncSi configurations in dielectric matrix. [36]

It is important to note that the conductivity of ncSi embedded in SiO<sub>2</sub> strongly depends on the degree of connectivity between silicon nanocrystals. Although the ideal isolated ncSi with well-defined size exhibits strong quantum confinement, the extremely low free carrier conduction caused by large ncSi spacing prohibits its applications in functional photoelectronic and photovoltaic devices. The charge transport in the ncSi/SiO<sub>2</sub> system is only achievable by increasing the quantum mechanical transparency through the potential barrier, hence, a stronger ncSi coupling is needed. This coupling can be achieved if silicon nanocrystals are closely packed or in intimate contact with each other. This kind of ncSi is described as touching or percolation ncSi as shown in Figure 1.10. [36] For the ncSi formed by solid-state crystallization in dielectric matrix, it has been shown that a percolation threshold for carrier conduction is about 40% excess silicon. This high excess silicon content tends to form larger ncSi with reduced quantum confinement effects and also cause difficulties in the control of the ncSi size and shape. Therefore, the approach of a superlattice structure for ncSi fabrication providing extra control on ncSi size becomes necessary.

In fact, this simple tunnelling model cannot fully describe the generally observed current-voltage (I-V) characteristics of the intrinsic ncSi/SiO<sub>2</sub> system, such as the temperature-dependent I-V characteristics and the high electric field I-V characteristics. Therefore, other transport mechanisms need to be considered to explain the complicated carrier transport in ncSi.

Based on the temperature-dependent characteristics of the conductivity, the activated hopping conduction mechanism is proposed as a dominant effect when the nanocrystal separation is larger and at temperatures above 100K. However, the hopping conduction usually requires an ohmic I-V behaviour, which can only be observed in low electric field conditions. Owing to the absence of a suitable model for high electric field behaviour, the Poole-Frenkel emission model is often employed showing current density behaviour as follows:

$$J \propto E \exp(\frac{q \ a\sqrt{E}}{kT \ \varepsilon_r}) \tag{1.9}$$

However, the disagreements in fitting parameters and trends in  $J \sim \sqrt{E}$  as a function of different silicon excess concentration (different  $\varepsilon_r$ ) cast into question the suitability

of this model. [37] Alternatively, the space-charge-limited current model can better interpret the I-V characteristics of ncSi in the presence of high electric fields. Considering the low-carrier concentration, it is reasonable that the strong carrier injection at high electric fields causes the formation of space charge to dominate the current density. The current density behaves as  $J \propto V^m$  and the exponent m is a parameter that describes an exponential trap distribution below the mobility edge. [38] Gutsch et al. propose the transport mechanism underlying the space charge limited current in intrinsic ncSi as a two-step defect-assisted band-to-band transition where the silicon surface dangling bonds are involved in carrier transition. The defectassisted transport is evident from the reduced current density after hydrogen passivation, which is well known to reduce the density of dangling bonds (DB) at ncSi surface. [37]

When dopants are introduced in ncSi, the carrier transport mechanisms are changed, resulting in dramatically improved conductivity. The dopants localised in SiO<sub>2</sub>, at ncSi interface and inside ncSi will all be critical for electrical conduction in doped ncSi.

Rather than working as donors or acceptors, the dopants in  $SiO_2$  work as deep-level defect states that reduce the transport barrier height, enhancing the tunnelling transport through the oxide. Theoretical h-DFT calculation show that P in  $SiO_2$  reduces the transport barrier height for electrons and holes by 97% and 85%,

respectively. [32] The dopants at ncSi interface tend to show dangling bond passivation effect before saturation. However, the excess dopant aggregation at interface will generate additional defects, which will cause stronger scattering to reduce the carrier mobility. [23, 39] The dopants inside ncSi will introduce majority carriers at high-doping level, which further enhances the electrical conduction. The band-conduction model is generally assumed for highly doped ncSi. However, the changes in the activation energy extracted from the Arrhenius fitting is a strong function of doping concentration and the reduced activation energy at lower temperature disagree with the band conduction assumption. Therefore, the carrier transport of doped ncSi is still in debate and requires further investigations.

# 1.5. Thesis aims and outlines

This thesis has three main aspects:

- 1. The investigation of plasma enhanced chemical vapour deposition (PECVD) for the silicon nanocrystals fabrication and photovoltaic devices fabrication.
- 2. The development of capacitance-voltage technique to characterise doping effects in highly resistive boron-doped ncSi embedded in SiO<sub>2</sub>.
- 3. Pulsed KrF excimer laser dopant activation in ncSi to improve doping efficiency.

**Chapter 1** reviews the basic principles of quantum confinement, the energy conversion efficiency limits and the all-silicon tandem solar-cell concepts. Experimental and theoretical research on the doping and carrier transport in ncSi embedded in SiO<sub>2</sub> is summarised and discussed. A summary of complex theoretical and technological challenges in ncSi doping and functional ncSi based photovoltaic devices is presented.

Chapter 2 describes the relevant material synthesis techniques as well as the characterisation methods used in this thesis.

**Chapter 3** begins with the optical, structural and chemical characterisations of the silicon-rich oxide (SRO) fabricated by PECVD, followed by an investigation of boron (B) and phosphorus (P) doping effects. After the demonstration of ncSi preparation by PECVD, ncSi-based single-junction photovoltaic devices are eventually fabricated and analysed. The device fabrication processes and possible improvements are presented. Diode I-V characteristics are shown and the best open-circuit voltage of 230mV is achieved. However, the parameters extracted from electrical measurements on this material indicate that the photovoltaic performance is still limited by the low-current transport and the strong non-radiative recombination. The expected superior material quality produced by PECVD (compared to sputtered material) does not exhibit improved photovoltaic performance. These limiting factors are attributed to

the ineffective doping in ncSi, which is a general problem for nano-semiconductor materials.

**Chapter 4** reviews the development of capacitance-voltage (C-V) measurement to investigate the boron-doped ncSi with high resistivity by using an inverted metal-oxide-semiconductor structure. It is demonstrated with the vertical current flow in these structures, is possible to avoid the complications that arise from the effects of lateral current flow and high-sheet resistance from standard MOS structures. The unique characteristic MOS CV results of doped ncSi are analysed and discussed. CV modelling is adapted to these structures to quantify electrical properties such as doping concentration, doping type and interface trap density distribution. Coupling these results with more detailed structural and electrical characterisations, the doping limitations of ncSi using Boron are identified and potential improvements are discussed. This C-V technique is potentially applicable to other doped nanocrystal materials to investigate doping.

**Chapter 5** presents developments in the annealing process to improve ncSi doping. It demonstrates that a pulsed KrF excimer laser ( $\lambda$ =248 nm,  $\tau$ =22 ns) can be used as a post-furnace annealing method to greatly increase the electrically active doping concentration in nanocrystal silicon (ncSi) embedded in SiO<sub>2</sub>. The application of a single laser pulse of 202 mJ/cm<sup>2</sup> improves the electrically active doping concentration by more than one order of magnitude, while also improving the conductivity. Using AFM and micro-Raman spectroscopy, it is also confirmed that there is no film ablation or significant change in ncSi structure. We propose and discuss interstitial P/B dopant activation to explain the improved electrical properties. Evidence of mobility-limited carrier transport and degenerate doping in the ncSi are measured with temperature-dependent conductivity, which further reveal the carrier-conduction mechanism in doped ncSi.

**Chapter 6** concludes the thesis by discussing the significance of the obtained results and developed techniques for research on silicon nanocrystals for photo-electronic applications. Directions for future research are suggested as well.

# **Chapter 2**

# **Experimental Details**

**Overview:** This chapter serves as the overview of fabrication and characterization techniques used in this thesis. In the first part, we specified the superlattice approach, RF-sputtering and plasma enhance chemical vapour deposition (PECVD) techniques and thermal/laser annealing methods for preparation of doped nanocrystal silicon in  $SiO_2$  matrix. The advantages and limitations of fabrication processes are summarized and discussed. The second part in this chapter focuses on the experimental details of the key characterization methods for the investigations of ncSi structural, electrical and optoelectronic properties.

# 2.1. Fabrication of Silicon Nanocrystals

With decades of research of silicon nanocrystals (ncSi), the preparation of ncSi mainly involves low-dimensional structure, thin film deposition and annealing for Si crystallization. The superlattice (multilayer geometry) structure has become the main stream approach to fabricate ncSi embedded in SiO<sub>2</sub> for the advantage of independent control on the ncSi size and density, The superlattice structure can be achieved by both radio-frequency (RF) magnetron co-sputtering disposition and plasma enhance chemical vapour deposition (PECVD), provided with accurate control of ultra-thin film thickness (normally 2-4 nm), SiO<sub>x</sub> stoichiometry and dopant involvement. However, the deposition process details of these two thin-film deposition methods are different. Additionally, the difference in terms of chemical composition of SiO<sub>x</sub> materials fabricated is also realized and discussed. Finally, the thermal annealing, including tube furnace and rapid thermal annealing, are illustrated with process details. The pulsed laser annealing method is also presented and discussed in terms of applications on ncSi fabrication.

#### **2.1.1.** Superlattice approach for size-controlled silicon nanocrystals

The silicon nanocrystals embedded in  $SiO_2$  are usually fabricated in nonstoichiometric silicon oxide or silicon rich oxide (SRO) by phase separation, silicon clustering and crystallization during high temperature annealing. [6, 40, 41] However, the broad size distribution [42] and the shape distortion [43] shown in ncSi formed in a single layer of SRO complicate the control of quantum confinement effects, which is undesirable for application to photovoltaic and photoelectronic devices.

In order to improve the control on the size and shape of ncSi, the superlattice (SL) approach proposed by Zacharias et al. (2002) has been verified and widely accepted.

[44] The schematic of the superlattice structure is shown in Figure 2.1. The superlattice consists of alternating thin film SiO<sub>2</sub> and SRO layers deposited on silicon or quartz substrates so that the growth of silicon crystals in SRO layers can be constrained by SiO<sub>2</sub> barrier layer. Therefore, the ncSi size becomes controllable by precisely tuning the SRO thickness. However, the ncSi density, the connectivity and the in-plane size are mainly determined by the excess silicon content in the SRO. The superlattice approach has been widely adopted to fabricate size controllable ncSi in SiO<sub>2</sub>, which can be clearly identified by high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and atom probe tomography (APT).



**Figure 2.1:** Schematic of as-deposited a-SiOx/SiO2 superlattice film and structure of Si nanocrystals embedded in SiO<sub>2</sub>.

Although the  $SiO_2$  layer thickness larger than 4nm is favoured to constrain the ncSi growth to form well isolated sphere-like ncSi, the vertical electrical conduction will be totally eliminated due to the nature of insulating  $SiO_2$ , even with impurity doping.

[36, 45] A SiO<sub>2</sub> thickness of 1.5nm - 2 nm has been used in this thesis as a compromise between acceptable electrical conductivity and ncSi size distribution.

#### 2.1.2. Radio-Frequency magnetron co-sputtering deposition

The RF magnetron sputtering is a physical vapour deposition (PVD) technique widely used for thin film deposition in the microelectronics and display industries for good film uniformity, precise rate control and various available materials. [41] In this work, a computer controlled AJA ATC 2200 sputtering system has been used for silicon rich oxide and SiO<sub>2</sub> depositions. (Figure 2.2) The capability of the precise control on silicon content (stoichiometry of SRO) and thin film thickness (1nm - 4nm) makes this deposition technique ideal for the ncSi superlattice fabrication.

As shown in Figure.2.2, the  $Ar^+$  ions from the magnetron confined gaseous Ar plasma is generated by13.56 MHz RF or DC power, in order to bombard the source material target in a high vacuum chamber (~3 x 10<sup>-7</sup> Torr). The target material particles ejected due to the high energy Ar+ bombardment will evaporate and finally reach the substrate placed in the path of the ejected ions. Then the evaporated target material solidifies on the substrate surface as a thin film coating. By controlling the RF/DC power, target tilting angle, substrate heating and precursor gas sources, the magnetron RF sputtering deposition provides a versatile tool to achieve variable thin film material properties.



**Figure 2.2:** Schematic diagram of the RF magnetron sputtering system used for sample fabrication. [46]

To be more specific on the deposition process, the  $SiO_2$  is deposited by using the pure  $SiO_2$  target and the silicon rich oxide is deposited by co-sputtering Si and  $SiO_2$  targets simultaneously. The SRO silicon content (stoichiometry) can be controlled by the ratio of Si and  $SiO_2$  deposition rates. The superlattice structure is achieved by

controlling the shutters on the targets with programmable process control software. Before superlattice deposition, the Si and SiO<sub>2</sub> deposition rate are calibrated in order to achieve repeatable Si%. The calibrated deposition rates of SiO<sub>2</sub> and Si are 8~10 Å/min and 15~20 Å /min. The very low deposition rates make the precise control on 1-2 nm thin film deposition possible.

For doping ncSi, dopants of boron (B) and phosphorous (P) are introduced during SRO deposition, by sputtering from Boron and  $P_2O_5$  targets respectively. The doping concentration is proportional to the power applied on the dopant targets.

The main advantages of magnetron sputtering are the precise control on the deposition rate and the SRO stoichiometry, the achievable high doping concentration (>  $10^{+20}$  cm<sup>-3</sup>) and the excellent film uniformity. However, with respect to the film quality, more voids and defects usually appear compared to Chemical Vapour Deposition (CVD), and it is also rare to get epitaxial growth by PVD unless using very high substrate temperature. [47]

## 2.1.3. Plasma enhanced chemical vapour deposition (PECVD)

The chemical vapour deposition (CVD) involves gas-phase chemical reaction directly on the substrate surface which is able to achieve dense and more adhesive thin films with fewer defects. [48] However, the temperature for chemical reaction is generally over 800 °C. By using a plasma the necessary energy for chemical reaction can be supplied at a much lower temperature, making fast chemical deposition possible at low temperature around 400 °C. The superior SRO and SiO<sub>2</sub> film quality fabricated by PECVD, compared to magnetron RF-sputtering, could be beneficial for ncSi based photovoltaic device performance improvement.



**Figure 2.3:** (a) The plasma enhance chemical vapour deposition system used for ncSi fabrication. (b) The schematic diagram of the capacitively coupled RF plasma deposition system.

The PECVD system utilized for the ncSi superlattice deposition in this thesis is a manually operated RF-PECVD cluster tool system manufactured by MV Systems, USA. The deposition is achieved by introducing reactant gas precursors between the parallel capacitively coupled electrodes with one grounded and the other one RF-energized, as shown in Figure 2.3 (b). The reactant gas precursors will be excited into plasma containing high energy ions and metastable molecules, which induces chemical reactions resulting in thin films being deposited on the substrates placed on the grounded electrode.

The pure SiH<sub>4</sub> and the N<sub>2</sub>O reactant gases have been used for the deposition of silicon dioxide (SiO<sub>2</sub>) and silicon rich oxide (SRO) films. The silicon content is mainly controlled by the gas ratio of SiH<sub>4</sub> and N<sub>2</sub>O. However, as the chemical reaction in plasma can also be dramatically influenced by other deposition parameters such as deposition pressure, RF power density, substrate temperature and total gas flow rate, it is important to optimize these parameters in order to control deposition rates and material stoichiometry. More details will be discussed in **Chapter 3**. Basically, the SiO<sub>2</sub> deposition rate is controlled at about 6 nm/min and SRO deposition rate is 10 nm/min. The doping gas sources used for boron and phosphorus doping were the 0.6 mol% Trimethylborane [TMB, B(CH<sub>3</sub>)<sub>3</sub>] diluted in H<sub>2</sub> and the 0.6 mol% PH<sub>4</sub> diluted in SiH<sub>4</sub> respectively.

Due to the nature of the gas reaction under vacuum conditions, the gas precursor environment in the vacuum chamber cannot change fast enough for the deposition transition between SiO<sub>2</sub> and SRO to form a distinct interface. Therefore, it is necessary to utilize a venting-refilling process between layer depositions in order to achieve the superlattice structure with sharp interfaces between SiO<sub>2</sub> and SRO layers. After each layer deposition, the chamber is vented for 5-7 mins until the base pressure 5 x 10<sup>-7</sup> Torr is reached again. Then the chamber will be refilled with the gas precursors for the next layer and the deposition starts when then process pressure is stable again. The sharp interface can be clearly identified in the Bragg peaks shown in the X-ray reflectivity (XRR) results (Figure 2.4).



**Figure 2.4:** The XRR result for a superlattice structure consisting of 20 bilayers (4 nm SRO/2 nm SiO2). The bilayer thickness evaluated from the Bragg peaks is 5.7 nm.

#### 2.1.4. Thermal annealing process

The formation of ncSi in SiO<sub>2</sub>/SRO superlattice can be generally achieved by high temperature thermal annealing at or above 1100 °C. During the annealing process, precipitation, clustering and crystallization of excess silicon occur in the SRO layer due to phase separation of Si and SiO<sub>2</sub>. [40, 41] As a consequence, the homogeneous SRO material becomes a mixture of silicon nanocrystals embedded in stoichiometric SiO<sub>2</sub> with thin SiO<sub>x</sub> interface regions. [36]

The quartz tube furnace annealing using  $N_2$  purging gas is the primary annealing method in this thesis. The  $N_2$  ambient can prevent the oxidation of excess silicon in

SRO during long time high temperature annealing. Before loading the as-deposited samples in the tube furnace at 600 °C standby temperature, the sample surface is cleaned by a standard RCA and HF dip process to remove all possible contaminants. The annealing process consists of 30 mins ramping up to 1100 °C, 1-2 hour annealing at 1100 °C or 1150 °C and then 1 hour ramping down to 600 °C before unloading samples from the tube furnace.

Rapid thermal annealing (RTP) is another thermal annealing method applied in this thesis. The main advantage of RTP over furnace annealing is the low dopant diffusion due to the fast heating and cooling rates and the total annealing time merely in minutes rather than hours. The prevention of dopant redistribution is significant for junction device fabrication. The RTP system utilizes a halogen lamp array for heating and Argon gas for purging. The temperature of the substrate is measured using a thermocouple. The temperature is ramped up at 7 °C/sec to the maximum temperature at 1100 °C. The annealing duration is 40 sec at 1100°C, followed by ramping down at the rate at 4 °C/sec. The total process time is approximately 8 mins.

#### 2.1.5. Pulsed laser annealing process

Pulsed laser annealing (PLA) has been widely applied in microelectronic fabrication. [49-52] The unique properties of pulsed laser in material processing are the very high achievable temperature (over 1450 K) and the extremely fast heating and cooling rate (~ $10^{+10}$  K/s), making its annealing effect very different from thermal annealing methods. [53] However, the investigation of pulsed laser annealed SRO has revealed that film ablation and low crystallinity mean that PLA is not a suitable annealing process for silicon nanocrystal fabrication. [51]

Although the pulsed laser may not be suitable for ncSi formation due to the strong film ablation of as-deposited SiO<sub>2</sub>/SRO superlattice, it still has potential for the modification of ncSi doping. For example, one of the PLA applications is to achieve the high doping density exceeding the dopant solubility limit in ion-implanted silicon, which cannot be achieved by traditional thermal annealing methods. [53, 54] Rather than suppressing the self-purification effect during furnace annealing, the results shown in Chapter.5 will demonstrate that a post annealing process using pulsed laser is able to trap and activate more dopants in ncSi, so as to improve the doping efficiency.

#### 2.2. Characterization Methods

Chemical, structural, electrical and optoelectronic characterization methods, including Fourier transform infrared spectroscopy, photoluminescence, X-ray diffraction, Raman spectroscopy, Hall effect, current-voltage and capacitance-voltage tests and atom probe tomography, have been used to investigate the properties of ncSi and ncSi based devices in this thesis.

#### 2.2.1. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a fast and versatile characterization tool widely applied to identify the chemical compositions in solid, liquid or gaseous materials. The application of the Michelson interferometer combined with the Fourier transform calculation enables the extraction of high resolution absorbance results from interferograms much faster than for dispersive spectrometers. [55] By identifying the specific infrared absorbance peaks due to characteristic molecular vibrations, the information of specific chemical bonds or molecular groups can be revealed. For example, the silicon oxide materials exhibit three main vibration peaks, representing Si=O stretching, bending and rocking modes, which can be found in the regions of 1050-1080 cm<sup>-1</sup>, 800-815 cm<sup>-1</sup> and 460-465 cm<sup>-1</sup> respectively. [56] As SiH<sub>4</sub> and N<sub>2</sub>O are used in PECVD deposition, the Si-H and Si-N bonds are inevitably present and are identified in SRO materials by FTIR. [57]

More detailed compositional properties reflecting the local chemical changes due to SRO stoichiometry and thermal annealing are presented in **Chapter 3**.

In this thesis, the FTIR measurement has been carried out using a Nicolet 6700 FTIR from Thermo Scientific in transmission mode. In FTIR measurement, the sample is placed normal to the IR light beam in a N<sub>2</sub> purged chamber. A detection range of 400-2000 cm<sup>-1</sup> and a resolution of 4 cm<sup>-1</sup> are used. For each sample, the absorbance data are the average result of 20 measurements to reduce the noise. Before FTIR measurement, 10 minutes N<sub>2</sub> purging time was carried out to minimize the absorbance in the range between 1400 cm<sup>-1</sup>– 1800 cm<sup>-1</sup> from CO<sub>2</sub> and H<sub>2</sub>O.

It is important to use a substrate with minimal IR absorption, especially in the SRO fingerprint region between 400 cm<sup>-1</sup> -2500 cm<sup>-1</sup>. Although Potassium bromide (KBr) is the ideal substrate for its low IR absorption, the low melting point of KBr substrate at 750 °C make it undesirable for ncSi materials because of the high temperature annealing. Si wafer is a good alternative substrate for its acceptable low IR absorption in the fingerprint region, and stability at high temperature. The characteristic absorbance from the thin film layer can be achieved by subtracting the silicon substrate absorbance for the measured sample absorbance data. For each sample, the silicon substrate is prepared and measured by FTIR to obtain the specific silicon substrate absorbance for subtraction.

In order to reduce the non-ideal features from the silicon substrates, double-sided polished Si wafer is necessary to avoid surface scattering, which will cause significant signal loss. Additionally, it is important to use low doped Si wafer (resistivity >10  $\Omega$ .cm) to prevent free carrier absorption. However, a baseline correction is still necessary to remove the offset usually shown in the FTIR absorbance spectrum. There are several factors that determine the baseline shift, such as scattering, reflection and apparatus configuration. The scattering happens when the wavelength of the IR light is comparable to the scale of surface roughness, which usually produces a stronger absorbance result with higher wavenumbers. In contrast, reflectivity is stronger for IR light with lower wavenumbers, which will be measured as stronger IR absorbance at lower wavenumbers. [58]

## 2.2.2. Photoluminescence

Photoluminescence (PL) is the most commonly used non-destructive technique to investigate the optical transitions in semiconductor nanocrystal materials. [10, 59-61] Although the exact mechanism of PL from ncSi is still under debate, PL results are generally used to evaluate the bandgap of ncSi materials. [10] Under excitation with photon energy higher than the material's bandgap, electron hole pairs are generated. After carrier thermalization to the conduction (electrons) and valence (holes) band edges, the electron and hole pairs undergoes radiative recombination. As the result of photoexcitation and radiative recombination, the photon emission energy reflects the bandgap energy distribution of nanocrystals. The blue shift in PL spectrum with reduced nanocrystal size is regarded as being the result of quantum confinement increasing their effective bandgap.

In this thesis, the photoluminescence (PL) has been measured at room temperature by a <sup>1</sup>/<sub>4</sub> meter monochromator (CornerstoneTM 260i) equipped with a silicon CCD camera at -30 °C using a 10 seconds integration time. The excitation source is a 50mW solid state 405nm (blue) CW laser source with a spot size of 0.5mm diameter. The PL spectra are corrected for the spectral response of the system and the PL data intensity directly describes the sample's emission intensity per wavelength interval.

#### 2.2.3. X-Ray Diffraction

X-ray Diffraction (XRD) is a non-destructive technique to characterize the structural properties of crystalline materials. For silicon nanocrystals, XRD can not only identify the existence of silicon crystallites, but it also reveals other useful information such as crystal orientation and average nanocrystal size.

The XRD measurement on ncSi has been carried out on a PANalytical Xpert Material Research Diffractometer (MRD) system using Cu K-alpha X-ray ( $\lambda$ =0.15418 nm). The incident beam is defined by a <sup>1</sup>/<sub>4</sub> divergent slit and a parabolic X-ray mirror. The receiving optics consist of a parallel plate collimator of 0.27° (0.0047 radian) acceptance angle and a Soller slit of 2.29° (0.04 radian) aperture. The diffracted X-

ray is measured by a single channel proportional detector. Due to the low diffracted X-ray intensity from the thin film ncSi with low atomic numbers, the XRD has been configured in the grazing incidence angle mode. After the sample alignment, the 1-3 degree Omega scan at  $2\theta$ =28.4° has been used to find the optimal incident angle. With this incident angle then fixed, a full range 2 $\theta$  scan is carried out. The existence of ncSi can be confirmed by the broad diffraction peaks at 28.4°, 47.4° and 56.3°, representing the Si crystal planes (111), (220) and (113) respectively.

The ncSi size can be estimated by the Debye-Scherrer equation. [62, 63] It has been found that the XRD diffraction peak is broader when the crystal size decreases to 100nm or lower because the acceptance angle for X-rays that satisfy the Bragg condition is larger.

$$L = \frac{K\lambda}{B\cos\theta_B} \tag{2.1}$$

, where, L is the crystal size, B is the integral breath or FWHM and  $\lambda$  is the X-ray wavelength. K is the Scherrer constant to be varied according to different shapes of crystals. The selection of K was amply discussed by Langford in 1978. [62] The K=0.89 is generally applied assuming a spherical ncSi shape.

In the case of ncSi with size lower than 5-6 nm, the ncSi size calculated by the Debye-Scherrer formula is quite consistent with the size observed under TEM. [64] But the Debye-Scherrer method will underestimate the size if the crystal size increases to

10nm or larger. This is because of the micro-strain representing the inhomogeneous lattice distortion. The least square relationships can be used to fit the broadening as a function of diffraction angle [65]:

$$B^{2}(2\theta) = \left(\frac{\kappa\lambda}{L\cos\theta}\right)^{2} + (4\varepsilon_{0}\tan\theta)^{2} + (B_{i})^{2}$$
(2.2)

The parameter  $\varepsilon_0$  in the second term represents the degree of micro-strain and  $B_i$  in the third term represents the instrumental broadening. The instrumental broadening can be calibrated for each angle and eliminated from the calculation. However, for the XRD measurement of ncSi in nm scale, this contribution from the diffraction instrument has been generally ignored.

#### 2.2.4. Raman spectroscopy

Raman Spectroscopy is another vibrational spectroscopic technique for the characterization of the crystalline quality of materials. The basic idea is to measure the energy difference between the incident and the re-emitted photons, which is the Raman shift in cm<sup>-1</sup>, due to the inelastic photon scattering with crystalline lattice standing wave vibrations, quantised as optical phonons. As the crystalline phonon lattice vibration energy shifts with the local crystal atomic arrangements, the Raman spectroscopy is widely used to investigate the details of crystallinity, residual stress and nanocrystal size of silicon nanocrystals. [66, 67]

The Raman shift results in this thesis have been obtained by using a Renishaw RM2000 micro-Raman spectrometer in a backscattering configuration. The laser source is a 25mW green laser (Ar laser) with wavelength  $\lambda$ =514.4nm. Before each measurement, the laser beam is carefully focused on the sample surface with an x50 objective lens. The laser beam size is confined to an area of 2 µm<sup>2</sup> and the power arriving at the sample surface is approximately 10mW at 100% laser power. In order to minimize the heating effect from laser illumination, the system has been configured at 1% laser power, 1s exposure time and 20 scans. Raman calibration has been performed using a crystalline silicon reference wafer exhibiting a narrow optical-phonon band peaked at ~520 cm<sup>-1</sup>

The most significant application of Raman spectroscopy for silicon nanocrystal characterization is the evaluation of the degree of crystallinity, which is indicated by the average percentage of the crystalline part in the silicon nanocrystals. [68] The Raman spectrum of annealed ncSi embedded in SiO<sub>2</sub> consists of a strong cSi related peak slightly red shifted from 520 cm<sup>-1</sup>, an asymmetric broadening of the peak on the low energy side due to a wider range of low energy phonons which are optically active in Si ncs and a broad shoulder extending to 400 cm<sup>-1</sup> from disordered interfaces and aSi.

The main peak around 520 cm<sup>-1</sup> is related to the Si crystalline longitudinal optical (LO) phonon mode. The asymmetric lineshape broadening and a peak shift to low

wavenumber (high frequency) are regarded as the consequences of phonon confinement, residual compressive stress and ncSi size distribution.

The disorder band ranging from 350 cm<sup>-1</sup> to 500 cm<sup>-1</sup> mainly relates to the amorphous Si phase. The characteristic peak at around 480 cm<sup>-1</sup> has been identified in amorphous silicon. Theoretically, three kinds of phonons may contribute this broad band: one is from disorder activated longitudinal acoustic modes (DALA) and the other two are from the disorder activated transverse optical (DATO) and longitudinal optical modes (DALO). Generally, one or two Gaussian-like distributions can fit this disorder band well. [68]

By fitting the Raman spectra using one asymmetric lineshape (crystalline) and two Gaussian-like peaks (amorphous), the crystallinity of annealed ncSi can be evaluated from

$$f_C = \frac{I_C}{I_C + \gamma I_a} \tag{2.3}$$

, where I<sub>c</sub> and I<sub>a</sub> are the integrated intensities of the crystalline and amorphous silicon phases, respectively.  $\gamma$  is the relative Raman cross-section of cSi with respect to amorphous Si due to the different Raman scattering efficiencies of both phases. For large or interconnected ncSi,  $\gamma$ =0.1 is generally used. [68] For the isolated ncSi with size about 2-4nm, the cross-section can be determined from the Raman spectra of low temperature annealed (amorphous) and high temperature annealed (crystalline) samples by considering the amount of amorphous phase transformed to crystalline phase. The cross-section of nanocrystallite silicon higher than 0.1 is generally reported. [69]

## 2.2.5. Electrical characterization

Static I-V measurement has been carried out on a probe stage equipped with an Agilent B2902a Source/Measure Unit (SMU) with excellent precision of 10fA/100nV sourcing and measuring resolution. The scanning DC voltage bias is from -1 V to +1 V with 0.1 V intervals. The current value is sampled after 100ms delay for each voltage bias for 500ms integration time. To minimize transient effects from charging and dielectric relaxation, the sweep rate of 0.1 V/s is used to ensure the steady state for each measurement.

The dynamic measurement is realized by the complex impedance measurement with the HP4234A impedance analyser. A sweeping DC gate voltage (Vg) has been applied to modulate the surface space charge region of the ncSi layer and a small AC signal has been used to measure the device impedance. As the space charge changes with the carrier redistribution by DC/AC electrical bias, the semiconductor capacitance changes and reflects the carrier dynamic properties. By analysing the capacitance of doped ncSi measured by capacitance voltage measurement (C-V), the doping type, electrical concentration, interface traps, flat band voltage and carrier dynamic properties in the doped ncSi can all be evaluated.

Thin film MOS devices have been fabricated by depositing electrically insulating  $SiO_2$  and an aluminium contact on top of the doped ncSi in  $SiO_2$ . The MOS structure under voltage bias is equivalent to a series connection of the oxide capacitance and the semiconductor capacitance. Then the semiconductor capacitance can be evaluated from the capacitance measured under accumulation and inversion conditions, depending on the electrode connection polarity and the sign of the DC bias. The voltage bias applied on MOS devices is from +30 V to -30 V with 0.1 V step size in order to show the full transition from accumulation to strong inversion. The sweep direction from +30 V to -30 V prevents influence from the undesirable discharging effects. For each measurement, 500ms delay time and a long integration time were used in order to make sure the measurement was carried out in equilibrium. The frequency characteristic can be evaluated by varying the AC frequency from 10 kHz to 1 MHz. And all the measurements have been performed in the dark.

#### 2.2.6. Hall effect measurement

The Hall Effect allows a relatively simple, low cost and fast electrical characterization tool to directly evaluate free carrier concentration, resistivity and carrier mobility. The physical principle of the Hall Effect is that the Lorentz force on moving carriers in a magnetic field makes charge accumulate on the side wall perpendicular to the current direction and the magnetic field direction. The charge accumulation stops when the electric force from the space charge induced electric field balances the Lorentz force:

$$-q \left( E + \nu \times B \right) = 0 \tag{2.4}$$

Where v is the carrier velocity, E is the transverse electric field and B is the magnetic field. The transverse voltage drop across the side walls is the Hall voltage ( $V_H$ ). The sign of the Hall voltage denotes the carrier type. If the current, magnetic field intensity and Hall voltage are known, the carrier density (n) can be evaluated from:

$$n = IB/q|V_H| \tag{2.5}$$

Then the Hall mobility can be evaluated when the resistivity ( $\rho$ ) is measured.

$$\mu = 1/(qn\rho) = |V_H|/\rho IB \tag{2.6}$$

Generally, the Van der Pauw resistivity measurement technique is used for thin film Hall measurement. (Figure 2.5)

It notes that the inhomogeneous film due to thickness, doping concentration and excess Si content will cause anomaly sign reversal and over-estimation of carrier concentration. In this thesis, the assumption of homogeneous film is used for Hall analysis so the measured carrier concentration can be regarded as the average upper limit.



**Figure 2.5:** The principle of Hall Effect for carrier concentration evaluation and the Van-der-Pauw contact for resistivity and thin film Hall measurement.

The Hall measurement in this thesis has been carried out by using the variable temperature HMS-5000 Hall system. Four gold probes are used with the sample measurable size from 3mm x 3mm to 15mm x 15mm. The magnetic field strength is 0.52 T. The temperature can be varied from 80K to 330K by using liquid N<sub>2</sub> cooling and up to 350K using a resistive heating stage. For each sample, I-V tests have been performed before Hall measurement to check that contacts are Ohmic with linear I-V curves. Multiple Hall measurements are carried out at different currents to confirm consistent resistivity and carrier concentration results.

## 2.2.7. Atom probe tomography

Atom probe tomography (APT) is a powerful technique to show the three dimensional atomic arrangement of a small sample with an extremely high spatial resolution of

several Angstroms. In this thesis, the atomic probe tomography data acquisition and image reproduction were carried out by Keita Nomoto. For doped silicon nanocrystals, APT can not only reveal the detailed silicon nanocrystal structure in a 3-D model, but can also identify the locations of dopant atoms, which determine the electrical and optical properties. [22] The correlation of the dopant local distribution results to the measured optical and electrical characteristics significantly help to further understand the mechanisms of optoelectronic transitions and carrier transport.

The principle of APT that atoms ejected from a needle-shaped specimen by application of an ablating voltage or laser, are detected by a position sensitive mass spectrometer together with their time of flight and positional information. The original elemental atomic arrangement can then be reconstructed by a geometrically based algorithms and models. In order to achieve the Angstrom spatial resolution, the monolayers of atoms are ionized and evaporated from a needle tip with a radius of less than 100 nm. The evaporation can be achieved by biasing the specimen with a high voltage with respect to the local ion collecting electrode. However, this approach only works well for conductive materials rather than semiconductors or insulators. Therefore, a UV pulse laser applied on the sample tip is generally used to replace the high voltage bias to supply sufficient energy for atom ionization and evaporation.

The APT measurements are performed on a LEAP 4000XSi (CAMECA) with a pulsed UV laser ( $\lambda$ =355 nm) for monolayer evaporation in a high vacuum chamber at
10<sup>-11</sup> Torr. The needle specimens are prepared using an Auriga FIB-SEM (Zeiss) by the typical lift-out method. [70] For the atomic monolayer evaporation by pulsed laser, the specimen holder is cooled to around 40 K with the laser pulse energy set at 100 pJ with a repetition rate at 250 kHz. The emitted atoms are accelerated and identified by the time of flight method. The position information is recorded by a Position Sensitive Detector (PSD) with a receiving efficiency of about 57%. With the data of position and atom type, the APT 3-D image can be reconstructed using the commercially available IVASTM software (version 3.6.6). The key parameters for the reconstruction are the field factor and the image compression factor (ICF), which have been carefully calibrated to ensure that the size and shape of features are consistent with TEM image results.

#### 2.3. Conclusion

This chapter outlines the key fabrication and characterisation techniques used in this thesis, including magnetron RF sputtering, PECVD, annealing, FTIR, XRD, Raman spectroscopy, PL, IV/CV tests and APT measurement. Not only the basic principles of these techniques have been presented, but the process details and measurement parameters are also included. The measurement results, analyses and discussions are described in the following chapters.

### **Chapter 3**

## PECVD Silicon Nanocrystal Fabrication and Tentative ncSi Based Photovoltaic Device

**Overview:** This chapter studies silicon nanocrystal materials fabricated by plasma enhance vapour deposition (PECVD) and its application on ncSi based photovoltaic devices. For the investigation of ncSi materials, not only the detailed experimental processes of PECVD deposition, annealing and doping are illustrated, but the chemical, optical and electrical properties of intrinsic/doped ncSi are presented and discussed. Compared with ncSi commonly fabricated by magnetron RF sputtering technique, some unique effects are investigated, including nitrogen and hydrogen involvements, chemical changes after thermal/RTP annealing and in-situ/ex-situ doping. To investigate the PECVD ncSi for photovoltaic application, the p-n and p-i-n diode devices have been fabricated and tested. Comparatively low solar cell performance is presented with the best open-circuit voltage of 230mV but no short-circuit current. These can be mainly attributed to low carrier transport, strong non-radiative recombination and low doping efficiency, which give rise to further investigations on doped ncSi in following chapters.

#### 3.1. Introduction

In recent years, a variety of fabrication techniques have been reported for preparing silicon nanocrystals embedded in SiO<sub>2</sub>, including ion-implantation [71], radio-frequency (RF) magnetron co-sputtering [72, 73] and plasma enhanced chemical vapour deposition (PECVD) [68, 74]. Generally, these deposition techniques are used for deposition of non-stoichiometric silicon oxide (silicon rich oxide or SRO) thin films covering composition ranges from silicon to silicon dioxide. The Si nanocrystals (ncSi) are formed by solid phase separation and crystallization in SRO during high temperature annealing. Compared to ion-implantation and RF-magnetron co-sputtering in terms of material quality, PECVD is favoured for the high quality SiO<sub>2</sub> [75], dense film with fewer voids/defects [76, 77] and good hydrogen passivation [78], which are potentially beneficial for better ncSi-based photovoltaic device performance. Additionally, to the best of the author's knowledge, no other ncSi based photovoltaic devices have been fabricated by PECVD.

In this chapter, plasma enhanced chemical vapour deposition (PECVD) is used to fabricate silicon nanocrystals embedded in  $SiO_2$ . In addition to the demonstrations of the ultrathin  $SiO_2/SRO$  film deposition and the excess silicon (stoichiometry) control in SRO, the material characterization results of SRO before and after annealing are presented with particular emphasis on the optical and chemical properties. To fabricate single junction photovoltaic devices, dopant impurities such as phosphorus

(P) and boron (B) have been used to form n-type and p-type ncSi, respectively. The ncSi *in situ* doped and the diffusion doping methods are investigated respectively, in terms of the electrical conduction and chemical composition. With the knowledge of ncSi fabrication and B/P doping by PECVD, initial prototype ncSi based photovoltaic diode devices are fabricated. The electrical characteristics and the photovoltaic performances of these diode devices are summarized and discussed. At finally, a lift-off device fabrication method without using RIE etching is proposed to avoid the over etching problem.

# 3.2. Basic stoichiometry control and chemical characterization of as-deposited SRO

The advantage of using the superlattice structure for ncSi fabrication, consisting of alternating silicon rich oxide (SRO) and SiO<sub>2</sub> bilayers, is the ease of control on ncSi size by simply tuning the SRO thickness. This can generally be achieved by accurately controlling the thin film deposition at a low growth rate. However, the in-plane ncSi structural features, such as nanocrystal lateral size, density and spacing, are determined by the stoichiometry of the as-deposited SRO layers. Therefore, it is more important to know how to control the stoichiometry by tuning the PECVD parameters.

It is found that the ratio of the SiH<sub>4</sub> and N<sub>2</sub>O flow rates is the most important PECVD parameter in controlling the stoichiometry. This directly relates to the material

refractive index. The refractive index can be accurately measured by Ellipsometry, being as a rapid optical characterization technique to evaluate the SRO film composition. As shown in Figure 3.1, the refractive index changes from 1.47 to 4.60 as a strong function of SiH<sub>4</sub>% ( $\frac{SiH4 \text{ flow rate}}{SiH4 + N20 \text{ gas flow rate}}$ ), indicating the transition from SiO<sub>2</sub> to amorphous silicon. Additionally, an almost linear trend can be observed above 50% SiH<sub>4</sub>%. For comparison, the refractive index results of as-deposited SRO with relatively high silicon richness (Si%=50%, 60% and 70%) fabricated by RF-sputtering are marked by the red dots in Figure 3.1. The similar results for refractive index mean that relatively high silicon content in SRO can be achieved by PECVD.



**Figure 3.1:** Refractive index of SRO fabricated at various SiH<sub>4</sub>% level. (The lines are a guide to the eye only) The Si% is calculated from the ratio of Si deposition rate and total Si+SiO<sub>2</sub> deposition rate during film preparation.

The other PECVD parameters, such as process pressure, RF power density and substrate temperature, are found to be mainly related to the deposition rate, material density and film uniformity, but still have some small effect on the stoichiometry [79]. To minimize these effects to the stoichiometry and keep the process repeatable, the process pressure, RF power density and substrate temperature are fixed after optimization for the purpose of low deposition rate and good film uniformity. The optimized process parameters are listed in Table 3.1. In this case, the stoichiometry can be solely controlled by SiH<sub>4</sub>% from 5% to 75%. The total flow rate is maintained in the low range of 10 sccm to 25 sccm (Standard Cubic Centimetre per Minute) (Table 3.2), which helps to keep a relatively low deposition rate. As also indicated in Figure 3.1, the deposition rates are stable at a low level about 9-11 nm/min for SiH<sub>4</sub>% from 20% to 75%, which makes it possible to accurately control SRO thickness for superlattice structure fabrication. The ultra-low SiO<sub>2</sub> deposition rate (SiH<sub>4</sub>%=5%) at about 5.6nm/min is achieved by using a low SiH<sub>4</sub> flow rate at 1 sccm and oversupplying N<sub>2</sub>O at 20 sccm.

Table 3.1: PECVD process parameters for lo	w deposition rate and film uniformity.
DECVD	Valaa

<b>PECVD</b> parameters	Value
Substrate temperature	400 °C
Base pressure	7x10 <sup>-7</sup> Torr
Process pressure	0.08 Torr
RF power density	$35 \text{ mW/cm}^2$

Table 3.2 SiH<sub>4</sub> and N<sub>2</sub>O flow rate and SiH<sub>4</sub>%

SiH <sub>4</sub> %	SiH <sub>4</sub> (sccm)	N <sub>2</sub> O (sccm)	Total (sccm)
5	1	20	21
20	5	20	25
33	5	10	15
50	5	5	10
58	7	5	12
67	10	5	15
71	12	5	17
75	15	5	20

In terms of chemical composition, an undesirable side-effect from PECVD deposition is the non-negligible nitrogen incorporation into the SRO film. The X-ray photoelectron spectroscopy (XPS) is applied on the as-deposited SRO film with refractive index of about 2.2 prepared using SiH<sub>4</sub>:N<sub>2</sub>O=5:8. The XPS system is Fisons ESCALAB220i-XL using a monochromatic Al K $\alpha$  x-ray radiation (1486.5 eV) and a hemispherical energy analyser. The chemical component of nitrogen can be clearly identified with a N-1s peak at a binding energy of 398.18 eV, as shown in Figure 3.2 (a). Further deconvolution of the Si-2p peak in Figure 3.2 (b) also reveals the strong  $Si^{3+}$  peak at 102.4 eV from Si-N, together with the Si-Si peak (Si<sup>0</sup>, 99.7eV) and Si-O-Si peak (Si<sup>4+</sup>, 103eV). [80] The integrated intensity peak areas of O 1s, Si 2p and N 1s peaks are used to estimate the relative elemental compositions after correction with core level atomic sensitivity factors. The more detailed material compositional results are summarized in Table.3.3. It shows that the nitrogen atomic concentration reaches 21.71 at. %, which is significant compared to oxygen (32.27 at. %). The silicon atomic concentration is around 41 at%, which is surprisingly consistent with SiH<sub>4</sub>%=38.5% calculated from the SiH<sub>4</sub>:N<sub>2</sub>O=5:8 ratio. Although the Si, O, N contents in SRO can be evaluated, XPS is not capable of detecting the element hydrogen, which should exist abundantly throughout the film.



Figure 3.2: XPS N1s and Si2p level results

Composition	Element	Binding energy (eV)	FWHM (eV)	Atomic concentration (%)
	C1s	285.00	1.41	6.46
	N1s	398.18	1.41	21.71
	O1s	532.89	1.76	31.27
Si-nitride	Si2p A	102.40	1.44	20.68
Si	Si2p B	99.65	1.29	5.76
Si-oxide	Si2p C	103.09	1.44	14.11

Table 3.3: SRO compositional details by XPS

The further evaluation of chemical composition of as-deposited SRO with various stoichiometries has been carried out by FTIR. The variation of chemical composition as a function of the SiH<sub>4</sub>:N<sub>2</sub>O ratio is shown in Figure 3.3. Compared to the SRO fabricated by RF sputtering, which only contains the elements silicon and oxygen, the SRO fabricated by PECVD exhibits more complex chemical compositions because of the additional involvement of the elements nitrogen and hydrogen. In Figure 3.3, the SiO<sub>2</sub> FTIR spectra from SiH<sub>4</sub>:N<sub>2</sub>O=1:20 is displayed as a reference only consisting of Si-O stretching (~1074 cm<sup>-1</sup>) and bending (~800-820 cm<sup>-1</sup>) modes.

In addition to the main absorbance peaks associated with Si-O stretching (1075cm<sup>-1</sup>) and bending (800-820cm<sup>-1</sup>) vibration modes, the Si-N stretching (850-890cm<sup>-1</sup>), Si-H

stretching (2200-2300 cm<sup>-1</sup>) and N-H stretching (3300-3400 cm<sup>-1</sup>) vibration modes are also clearly identified. However, no O-H bonds were detected around the 3600cm<sup>-1</sup> <sup>1</sup> range [81]. The more detailed chemical vibration modes are summarized in Table 3.4.



Figure 3.3: FTIR spectra of as-deposited SRO fabricated by PECVD

Wavenumber (cm <sup>-1</sup> )	Assignment of the infrared mode	Ref.
450	Out-of-plain Si-O rocking mode in SiO <sub>2</sub>	[82-84]
800-820	Si-O bending mode	[56, 83, 84]
850-890	Si-N stitching mode	[82, 85]
1050-1080	Si-O-Si TO stretching mode	[56, 83, 84]
1100-1200	A broaden shoulder band from TO asymmetric Si-O stretching mode	[83, 84]
2000-2160	Si-H stretching mode in Si-Si neighbouring	[82, 85-87]
2200-2300	Si-H stretching mode with N neighbouring	[85]
3400	N-H stretching mode	[82, 85]

Table 3.4: Assignments of the FTIR vibration modes

It is also found that the integrated absorbance peak area of Si-H is generally larger than that of N-H, even considering that the absorptivity of Si-H bonds is 1.4 times greater than the absorptivity of N-H. [88] As the chemical bond concentration is proportional to the approximate absorbance peak areas, the larger Si-H peak area indicates that hydrogen may be more preferentially bond to silicon than to nitrogen. As the silicon richness increases with higher SiH<sub>4</sub>:N<sub>2</sub>O ratio, there will be more silicon available to be linked to nitrogen, so that the Si-N stretching mode peak (850-890 cm<sup>-1</sup>) dramatically increases with the Si-O bending mode (800-820 cm<sup>-1</sup>) smeared out (Figure 3.3). However, since the bond energy of Si-O (799.5 kJ/mol) is higher than that of Si-N (470 kJ/mol), [89] Si-O bonds will be more likely to form than Si-N bonds, which is indicated by the generally stronger Si-O-Si peak at 1075cm<sup>-1</sup> for various SiH<sub>4</sub>:N<sub>2</sub>O ratios. Meanwhile, the stronger peak intensity of hydrogen related vibration modes (Si-H and N-H) can also be observed with increasing SiH<sub>4</sub>:N<sub>2</sub>O up to 5:5.



Figure 3.4: Si-H stretching mode peak shifts with SiH<sub>4</sub>:N<sub>2</sub>O ratio

Further increasing the excess Si will reduce the N content as the obvious decrease of Si-N and N-H vibration modes in the FTIR spectra from SiH<sub>4</sub>:N<sub>2</sub>O=12:5 and 15:5. This effect can be further confirmed by the detailed analysis on the Si-H stretching modes in Figure 3.4.

Generally considering the Si-H bonding of H to a Si site which is connected to the Si-Si bond network, the Si-H vibration (absorbance) peaks can be found in the regime of 2050- 2160 cm<sup>-1</sup> depending on whether one, two or three H atoms are at the Si site. [86] However, the frequency of the Si-H vibration modes will shift to higher wavenumbers due to the decrease in the Si-H bond length induced by replacing Si with a neighbouring N. [85] Therefore, as nitrogen content decreases, the clear Si-H stretching vibration mode shifts from 2250 cm<sup>-1</sup> to 2100 cm<sup>-1</sup>. The nitrogen related bond reduction is reasonable since the over-supply of silane (SiH<sub>4</sub>) will compete with the nitride molecular group to form a highly silicon rich local atomic structure.

#### **3.3.** Structural and chemical properties of the annealed SRO

#### 3.3.1. Identification of Silicon Nanocrystals

Silicon nanocrystals (ncSi) are generated by high temperature phase separation and Si crystallization in the SRO layer. The tube furnace annealing at 1100 °C in a  $N_2$  ambient for 1 hour has been applied to obtain highly crystalline and interfacially relaxed ncSi with reduced non-radiative recombination. [66, 90] This is desirable for

photovoltaic and photonic applications. The successful formation of Si nanocrystals in annealed SRO by PECVD can be directly confirmed by X-ray diffraction by identifying the characteristic Si Bragg diffraction peaks at 28.4°, 47.4° and 56.3° in Figure 3.5, for (111), (220) and (310) planes respectively. Higher excess silicon content achieved by using higher SiH<sub>4</sub>% results in the formation of a higher density of silicon crystallites, which contributes to a stronger diffraction peak intensity. The SiH<sub>4</sub>% is calculated from the SiH<sub>4</sub>:N<sub>2</sub>O ratio as SiH<sub>4</sub> flow rate /total flow rate. Additionally, the average feature size of ncSi also varies with silicon content. An empirical method using the Scherrer equation is applied to approximately quantify the average size of crystals by analysing the diffraction peaks.

$$g = \frac{K\lambda}{\Delta(2\theta)\cos(\theta)}$$
(3.1)

, where  $\lambda$ =0.154 nm,  $\theta$  is the Bragg diffraction angle at the peak position, K=0.89 is a correction factor for integral breadth of spherical crystals with cubic symmetry [62] and  $\Delta$ (2 $\theta$ ) is the full-width at half maximum (FWHM) of the corresponding peak at 2 $\theta$ .

By assuming a spherical ncSi shape, the calculated average ncSi feature size for SiH<sub>4</sub>% at 62%, 50% and 38% are  $5.7\pm0.6$  nm,  $5.5\pm0.5$  nm and  $4.1\pm0.5$  nm respectively. As expected, larger evaluated average size of ncSi is found in SRO with higher Si% due to higher excess Si content.



Figure 3.5: The X-ray diffraction results of silicon rich oxide by PECVD after 1100 °C furnace annealing in a  $N_2$  ambient for 1 hour. The SRO materials fabricated with various SiH<sub>4</sub>% were investigated.

#### 3.3.2. Nitrogen and hydrogen in annealed SRO

After high temperature furnace annealing, Si nanocrystals, formed through phase separation and silicon clustering, are affected greatly by the dramatic change in the chemical bond configuration. As shown in Figure 3.6, the most remarkable change after annealing is the reduction in the Si-N stretching mode peak around 850-890 cm<sup>-1</sup>. Additionally, a stronger Si-O-Si stretching mode peak (at 1070 cm<sup>-1</sup>) can be clearly identified to dominate the chemical composition of the annealed SRO films. These

results may indicate the formation of more N-O bonds in the dielectrics as  $SiN_xO_y$  and ncSi interfaces after phase separation and silicon clustering. The presence of nitrogen in the dielectric matrix, especially at the ncSi interface, will lead to significant structural, optical and electrical properties as compared to nitrogen free SRO materials prepared by RF-sputtering. [91]



Figure 3.6: FTIR spectra of PECVD SRO before and after 1100 °C furnace annealing

Firstly, the presence of nitrogen in SRO material will affect the phase separation during high temperature annealing. It has been reported that nitrogen will hinder the ncSi growth to form smaller ncSi size by either suppressing the silicon atom diffusion to form the ncSi during annealing [92] or consuming silicon by nitridation at the nanocrystal interface. [80] Di et al. have systematically investigated the ncSi structure by XRD and have shown that the silicon nanocrystal sizes formed by using SiN<sub>x</sub> barrier layer are smaller than using SiO<sub>2</sub> barrier layers. [93] Therefore, higher annealing temperature at 1150 or 1200 °C can be used not only for complete phase separation and crystallization of ncSi from nitrogen-incorporated SRO by PECVD, but also for enhancing nucleation and achieving higher ncSi density. [94, 95]

Furthermore, when the ncSi is formed in nitrogen-incorporated SRO by phase separation at high temperature, it is conceivable that the surrounding dielectric environment will contain nitrogen surface terminating groups, which changes the interface dielectric polarity. Therefore, the electronic structure is determined by both the quantum confinement (ncSi size) and the N incorporation. The N coverage at the ncSi interface can be beneficial to form higher ncSi bandgap, which is more prevalent for smaller ncSi where the interface generally dominates. [96] A comparison of experimental PL bandgaps of ncSi embedded in Si<sub>3</sub>N<sub>4</sub> showed increased bandgap with reduced size, significantly greater than that for ncSi of the same size in SiO<sub>2</sub>. [93, 97, 98] The DFT calculation on the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LOMO) energy gap of Si<sub>35</sub>(OH)<sub>x</sub>(NH<sub>2</sub>)<sub>y</sub> nanoclusters as a function of OH- and NH<sub>2</sub>- coverage also theoretically illustrates the increased  $E_{gap}(DFT)$  with increasing N interface coverage.[96, 99] However, it should be noted that this effect is insignificant for bigger nanocrystals (>4 nm).

Another significant change in SRO chemical composition after thermal annealing is the disappearance of Si-H and N-H vibration modes as a consequence of hydrogen effusion. Hydrogen effusion can be described as the breaking of Si-H and N-H bonds, the formation of more Si-O and Si-N bonds and the liberation of H ions.



**Figure 3.7:** The optical refractive index (a) and absorption coefficient (b). The increased absorption coefficients after furnace annealing (dashed lines) and RTP (dotted lines) are clearly indicated by the arrows shown in (b).

The presence of large amounts of hydrogen in as-deposited SRO is believed to be the most significant feature of PECVD because the defects/dangling bonds can be passivated very effectively by hydrogen. However, the inevitable high temperature annealing process, which is necessary for phase separation and silicon nanocrystal formation, causes strong hydrogen effusion. A significant fraction of liberated hydrogen is lost and in turn it can in itself produce large amounts of defects and

dangling bonds as stronger absorption. As shown in Figure 3.7, it is found that the material refractive index and the absorption coefficient increase after high temperature annealing, which is totally opposite to the annealing effect shown in the thermally annealed SRO material prepared by RF-sputtering or ion-implantation that the refractive index and the absorption coefficient decrease.

Generally, the as-deposited SRO materials fabricated by physical vapour deposition (RF-sputtering or ion implantation) contain a high density of voids, [79] defects and dangling bonds. The high temperature thermal annealing of  $SiO_x$  or  $SiO_xN_y$  in N<sub>2</sub> ambient will densify the materials to form silicon crystallites and remove dangling bonds. Therefore, reduced refractive index and lower absorption results are widely observed after annealing. [100]

In contrast, the higher refractive index and increased optical absorption observed in annealed PECVD SRO (Figure 3.7) indicate the transition from dangling bonds free to dangling bonds rich after thermal annealing. This can possibly be explained by the formation of more Si- or N- dangling bonds from the breaking of Si-H and N-H bonds after higher temperature annealing. However, there should be still a net defect passivation effect compared to ncSi by sputtering or ion-implantation.

It is noteworthy that the hydrogen in as-deposited SRO film by PECVD will not guarantee the improved material quality after annealing, but can generate more defects/dangling bonds due to H<sub>2</sub> effusion, compared to as-deposited samples. Hence whether there is a beneficial effect of the H in PECVD depends sensitively on the conditions. An additional hydrogen passivation process after high temperature annealing, such as forming gas annealing or hydrogen plasma treatment,[101] may well be more beneficial to actually improve the material quality. Using longer thermal annealing time at higher temperature such as 1150 °C to 1250 °C may also help.

#### 3.3.3. Rapid Thermal Annealing for Crystallization

Rapid thermal process has also been applied for silicon crystallization in PECVD SRO. The halogen lamp based RTP has been configured to anneal SRO samples in Ar ambient at 1100 °C for only 40s. There is no significant difference in refractive index observed between RTP and furnace annealing. As shown in Figure 3.7, the SRO materials annealed by RTP also exhibit increased refractive index and larger absorption coefficient which can be attributed to hydrogen effusion. This result also indicates the hydrogen effusion is a fast solid phase chemical reaction process at high temperature.



**Figure 3.8:** Raman spectroscopy results of PECVD SRO materials annealed by furnace annealing (a) and RTP (b)

In terms of ncSi formation, this 40s RTP annealing shows a similar degree of solid state crystallization compared to long time furnace annealing. As shown in Figure 3.8, the asymmetric Raman spectra of RTP annealed ncSi is consist of one strong Raman peak at 509 cm<sup>-1</sup> from silicon crystallites and a broad shoulder background (490 cm<sup>-1</sup> to 360 cm<sup>-1</sup>). Compared to the sharp c-Si Raman peak at 521 cm<sup>-1</sup>, the broad asymmetric peak at 509 cm<sup>-1</sup> and the 12 cm<sup>-1</sup> downshift can be due to the mixed contributions from local phonon quantum confinement, stress and smaller nanocrystal sizes. [68, 102] However, it should be noted that the samples annealed by RTP show relatively broader peak shoulder from 490 cm<sup>-1</sup> to 360 cm<sup>-1</sup> for the main peak at 509 cm<sup>-1</sup>. One possibility for this obvious shoulder can be the larger amorphous shells and highly disordered interfaces. [66] The wider distribution of small ncSi can also contribute to this shoulder background. [66, 103]

The ncSi formation during thermal annealing involves three solid phase reactions, including 1) phase separation of  $SiO_x$  by precipitation of Si in dielectric matrix, 2) Si atoms clustering/coagulation as size growth and 3) Si nucleation (crystallization). These processes are all thermally activated and probably happen simultaneously. [104]

In principle, higher temperature annealing (over 1000 °C) is essential for phase separation of  $SiO_x$  and high density of ncSi nucleation sites, especially for smaller sized ncSi formation [102]. There are several kinetic models can possibly explain the crystal nucleation mechanism, such as the homogeneous nucleation with a supercooling process [105] or the heterogeneous growth on nucleation seeds [106].

In terms of Si precipitation and coagulation, a diffusion-limited Si incorporation model is generally accepted. [107] However, this model cannot describe the fast phase separation in 1 s at 1200 °C and 20  $\mu$ s at 1350 °C as demonstrated by Kachurin *et al.* [52]. Additionally, the Si diffusivity in SiO<sub>2</sub> required to model the fast process has to be several orders of magnitude larger than the experimentally determined values. [108]

Sarikov *et al.* has proposed another new mechanism of local oxygen out-diffusion leaving Si atoms clustering and surrounded by a more SiO<sub>2</sub>-like matrix. [40] This mechanism describes the fast phase separation in a short time interval in seconds (< 1s) rather than in hours. If solely considering Si diffusion at 1200 °C, a prediction of complete separation of SiO<sub>x</sub> annealing time over 3 hours is illustrated. [40] Indeed, the rapid thermal annealing (RTP in seconds) [109] and the 20ms flash lamp annealing (FLA) [52] have been also experimentally demonstrated to form ncSi with comparable structural properties to long term furnace annealed ncSi. [110] The application of a fast annealing techniques can dramatically reduce the thermal budget in ncSi fabrication, reduce dopant diffusion in ncSi based devices and make it possible to use substrates that are not stable over long time high temperature annealing. However, one problem that arises from RTP or FLA is the high density of dangling bond/defects after annealing, which makes the ncSi inappropriate for photovoltaic or optoelectronics application. This can also be confirmed by the stronger disorder background shown in Figure 3.8 (b). Hiller et al. have compared furnace annealing, RTP and flash lamp annealing of PECVD ncSi in SiO<sub>2</sub> in terms of photoluminescence and experimentally summarized that the medium temperature post-annealing inert gas (Ar or N<sub>2</sub>) and forming gas (containing H<sub>2</sub>) passivation annealing remarkably remove defects/dangling bonds and regain the ncSi luminescence. [104] The regained PL luminescence intensity after forming gas annealing is comparable with traditionally furnace annealed ncSi.

#### 3.4. Boron and Phosphorus Doping in Silicon Nanocrystals

Doping ncSi to modify its electrical properties is essential in order to realize the ncSi based junction photovoltaics devices. In this sub-section, both boron and phosphorus

doping of PECVD ncSi are investigated. Besides in-situ doping as the general method foe ncSi, the diffusion doping is also presented as another possible doping method.

#### 3.4.1. In-Situ Doping

The in-situ doping in ncSi is achieved by including gas sources containing group III or group V impurity atoms in the silicon rich oxide during material deposition process. When the silicon nanocrystallites are formed during high temperature thermal annealing, the principle is that any impurity atoms which remain in the ncSi on annealing are simultaneously activated to generate majority carriers.

The boron (group III) and phosphorus (group V) impurities were used to form p-type and n-type ncSi respectively. The doping gas sources used in PECVD deposition were 0.6 mol% Trimethylborane [TMB, B(CH<sub>3</sub>)<sub>3</sub>] diluted in H<sub>2</sub> for boron doping and the 0.6 mol% PH<sub>4</sub> diluted in SiH<sub>4</sub> for phosphorus doping. Due to the equipment limitations on the doping sources concentration, the minimum stable flow rates (10 sccm of TMB and 6 sccm of SiH<sub>4</sub> (PH<sub>4</sub>)) were used in order to achieve the lowest resistivity testable by IV measurement. For SRO deposition, the maximum doping source (TMB or PH<sub>4</sub>) and N<sub>2</sub>O gas flow rates were fixed. Different SiH<sub>4</sub> flow rates were used to vary the SiH<sub>4</sub>:N<sub>2</sub>O ratio to control the excess silicon to form various ncSi feature size and interconnectivity. It is conceivable that dopant concentration will be diluted in PECVD precursor gases by using higher SiH<sub>4</sub> flow rates. Therefore, higher SiH<sub>4</sub>% will not only increase excess silicon content, but also reduce the doping concentration.



**Figure 3.9:** FTIR results of B and P doped SRO by PECVD. No chemical composition change due to doping can be observed.

In terms of chemical composition, there is no notable change observed in as-deposited SRO due to incorporation of boron or phosphorus impurities. As the FTIR results show in Figure 3.9, the characteristic Si-O, Si-N and Si-H vibration modes are identical with the intrinsic as-deposited SRO materials fabricated by similar SiH<sub>4</sub>:N<sub>2</sub>O

ratio (Figure 3.3). The refractive index values are in the range of 2.5 - 2.9 (Table 3.5), which are also consistent with intrinsic SRO fabricated by the same SiH<sub>4</sub>:N<sub>2</sub>O ratio (Figure 3.1).

The Circular-Transmission Line measurement (TLM) was applied to evaluate the resistivity of doped ncSi thin film after annealing. The schematic TLM pattern is shown in Figure 3.10.



Figure 3.10: Circular-TLM structure pattern.

The total resistance measured between the inner and outer contacts consist of the resistance of the ncSi material ( $R_{ncSi}$ ) and the contact ( $R_c$ ).

$$R_{total} \approx R_{ncSi} + 2Rc \tag{3.3}$$

$$R_{ncSi} = \int_{r_{in}}^{r_{out}} \rho_{sheet} \times \frac{dr}{2\pi r} = \frac{\rho_{sheet}}{2\pi} \ln(\frac{r_{out}}{r_{in}})$$
(3.4)

Therefore, by plotting  $R_{total}$  as a function of  $ln(r_{out}/r_{in})$ , the sheet resistivity and  $R_c$  can be calculated from the slope of the plot ( $\rho_{sheet}/2\pi$ ) and the intercept ( $2R_c$ ) respectively.

The more detailed IV measurement results are illustrated in Figure 3.11 for P doping and Figure 3.12 for B doping. The linear IV curve and TLM plots confirm the formation of ohmic contacts after the forming gas anneal, except for the 5um in P#3 which is hence eliminated from further TLM evaluation.



Figure 3.11: Detailed TLM results of phosphorus doped SRO after 1100°C annealing



Figure 3.12: Detailed TLM results of boron doped SRO after 1100°C annealing



Figure 3.13: The resistivity of B and P doped SRO after annealing as the function of SiH<sub>4</sub>%

The best B and P doped SRO samples showing remarkably reduced resistivity are listed in Table 3.5, which also includes the sheet resistance and contact resistivity. The successful doping can be confirmed by the reduced resistivity, compared with reported over M $\Omega$ .cm for intrinsic PECVD ncSi. [25] The lowest resistivity values achieved are 65.1  $\Omega$ ·cm at SiH<sub>4</sub>% = 54.5% for P doped ncSi and 188  $\Omega$ ·cm at SiH<sub>4</sub>% = 70.6% for B doped ncSi. It is obvious that the P doped ncSi generally show lower resistivity than B doped ncSi. However, the B and P doping in ncSi exhibit very different resistivity trends as a function of SiH<sub>4</sub>%. As shown in Figure 3.13, when the SiH<sub>4</sub>% increases from 54.5% to 70.6%, the B doped samples have shown remarkable reduction in resistivity from 5.36x10<sup>5</sup> to 1.89x10<sup>2</sup>  $\Omega$ ·cm, but the P doped samples show doubled resistivity increasing from 65 to 155  $\Omega$ ·cm.

The electrical conductivity ( $\sigma$ =1/ $\rho$ ) in ncSi is much more complicated than bulk silicon due to the complex structural and chemical properties of this cSi/dielectric hybrid system. To simplify the analysis, the conductivity can be generally described as  $\sigma$ =q·n· $\mu$ , which is determined by the free carrier concentration (n) and the carrier mobility ( $\mu$ ). The increase of SiH<sub>4</sub>% in the SRO PECVD deposition (Table 3.5) has two different effects on the electrical properties (n and  $\mu$ ) of doped ncSi:

(1) The higher SiH<sub>4</sub>% induces larger ncSi formation, narrower spacing between ncSi and even the possibility of interconnected ncSi networks, which will improve carrier mobility ( $\mu$ ). [36]

(2) The higher SiH<sub>4</sub> gas flow ratio will dilute the doping gas precursor concentration so as to reduce the dopant density (n) in SRO, which will increase the resistivity.

Gas ratio	SiH <sub>4</sub> %	Refractive index*	$R_{Sheet}$ ( $\Omega/\Box$ )	Resistivity^ (ρ) (Ω·cm)	ρ <sub>contact</sub> (Ω·cm <sup>-2</sup> )
SiH4:SiH4(PH4):N2O=0:6:5	54.5%	2.56	4.15x10 <sup>6</sup>	65.1	2.8x10 <sup>-3</sup>
SiH4:SiH4(PH4):N2O=2:6:5	61.5%	2.71	7.51x10 <sup>6</sup>	74.0	4.8x10 <sup>-3</sup>
SiH4:SiH4(PH4):N2O=6:6:5	70.6%	2.80	1.48x10 <sup>7</sup>	155.4	1.88x10 <sup>3</sup>
SiH <sub>4</sub> :N <sub>2</sub> O:TMB(H <sub>2</sub> )=6:5:10	54.5%	2.35	4.63x10 <sup>10</sup>	5.36x10 <sup>5</sup>	$2.37 x_{4}^{10^{+}}$
SiH4:N2O:TMB(H2)=8:5:10	61.5%	2.60	8.68x10 <sup>8</sup>	1.07x10 <sup>4</sup>	6.59x10 <sup>+</sup>
SiH <sub>4</sub> :N <sub>2</sub> O:TMB(H <sub>2</sub> )=12:5:10	70.6%	2.94	1.34x10 <sup>7</sup>	188.0	3.55x10 <sup>-1</sup>

Table 3.5: Optical and electrical properties of B and P doped SRO by PECVD

\* Refractive index at 600nm wavelength before annealing.

^ For comparison, intrinsic PECVD ncSi has resistivity over 1 MΩ.cm. [25]

The total resistivity vs. SiH<sub>4</sub>% and doping levels shown in Figure 3.13 could be the result of the combination of these two effects. For B doped ncSi the carrier transport ( $\mu$ ) is the major limiting factor because the resistivity dramatically deceases with higher SiH<sub>4</sub>% as indicated in (1). But for P doped ncSi, the doping concentration (n) reduction overweighs the increased carrier transport ( $\mu$ ) since the resistivity increases in a narrow range from 60  $\Omega$ ·cm to 160  $\Omega$ ·cm with higher SiH<sub>4</sub>% as described in (2).

One possible explanation of the observed result is that phosphorus enhances silicon crystallization in SRO so that larger or interconnected ncSi are formed in P doped SRO even at low SiH<sub>4</sub>%, so that carrier transport is improved and P doping is more effective. But B doped ncSi are in smaller size with large spacing so that carrier transport is the main limiting factor.

Similar results have been well reported for P and B doped SRO materials fabricated by RF magnetron sputtering, that P doped ncSi size tends to be larger and B doped ncSi size to be smaller, comparing to their intrinsic counterparts. [34, 35] The larger ncSi and interconnected ncSi network [22] can dramatically increase carrier transport, which fundamentally increases the conductivity in ncSi material. This also explains the much lower resistivity of P doped ncSi observed even at low SiH4% shown in Figure 3.13.

It is important to note that the ncSi crystallization process is inherently entangled with the dopant activation process in the *in situ* doping method, which makes it difficult to control the ncSi structural properties in terms of ncSi size and crystallinity.

#### **3.4.2.** Diffusion Doping Method

Compared to *in-situ* doping, the main advantage of diffusion doping is the separation of ncSi crystallization and the dopant diffusion/activation. As discussed in Section 3.3.3, the phase separation and crystallization of ncSi is a fast process which can be

completed in less than 1s if high temperature over 1100 °C is reached. However, the dopant diffusivity in dielectric material is extremely low so that the dopant diffusion will take a much longer time than ncSi formation. Therefore, the dopant diffusion and activation is expected to happen after ncSi formation, and so will have much less influence on Si phase separation and crystallization.



Figure 3.14: The sample structures for the diffusion doping method

The sample structures to investigate the diffusion doping method are shown in Figure 3.14. Rather than using N<sub>2</sub>O, a pure O<sub>2</sub> source has been used for SiO<sub>2</sub> and the SRO PECVD deposition, and SiH<sub>4</sub>:O<sub>2</sub>=2:1 was used to control the excess Si content in SRO. The external doping source is a 50nm SiO<sub>2</sub> layer containing an extremely high density of boron (B: p-type) or phosphorus (P: n-type). These doping layers were prepared by the RF-sputtering system before PECVD deposition, using a high Boron/P<sub>2</sub>O<sub>5</sub> sputtering rate during SiO<sub>2</sub> deposition. Then the thin film superlattice structures were fabricated by PECVD on top of the doping source layer. Besides the traditional SiO<sub>2</sub>/SRO superlattice structure, thin amorphous silicon layers less than

0.5nm were applied next to the SRO layer in order to increase the silicon richness for large ncSi to give better conductivity (Figure 3.14 (b), (c)).

The sheet resistance of undoped and boron/phosphorus doped ncSi have been measured by TLM as illustrated in Figure 3.15. The B/P doped ncSi both exhibit much lower sheet resistance than intrinsic ncSi, which confirms the feasibility of B and P doping by the diffusion method. However, the various superlattice structures do not show the expected trend in the sheet resistance. The boron doped ncSi generally shows lower sheet resistance than phosphorus doped ncSi, which can be explained by faster boron diffusion than phosphorus because it is a smaller atom. [111]



Figure 3.15: Sheet resistance of B/P doped ncSi by the diffusion doping method

#### 3.5. Tentative ncSi-Based Photovoltaic Devices by PECVD

#### **3.5.1.** Device Fabrication Process

The *p-n* and *p-i-n* diode devices were fabricated by PECVD deposition on quartz substrates. The schematic device structure is shown in Figure 3.16. The phosphorus doped region (n) and the intrinsic region (i) are in the superlattice structure consisting of alternating SiO<sub>2</sub>/SRO bilayers. The p-type region is a 25nm highly boron doped SRO monolayer. Two groups of devices were prepared with two SRO thicknesses of 3.5 nm and 4 nm in order to have different ncSi feature sizes. For each group, the number of intrinsic bilayers varies from 0, 10 20 and 30. The intrinsic bilayers were expected to have longer lifetime than doped bilayers. The sample parameters are listed in Table 3.6



Figure 3.16: The PECVD ncSi based p-i-n diode device structure.

Group#1	n-type region (P doped)	Intrinsic region (SRO:SiO <sub>2</sub> =3.5nm :1.5nm )	p-type region (B doped)
PIN1_0i	40 bilayers	0 bilayer	
PIN1_10i	SRO=3.5 nm	10 bilayers	25nm highly boron doped
PIN1_20i	SiO2=1.5nm	20 bilayers	SRO
PIN1_40i	Total 200nm	30 bilayers	
Group#2	n-type region (P doped)	Intrinsic region (SRO:SiO <sub>2</sub> =4.0nm :1.5nm )	p-type region (B doped)
Group#2 PIN2_0i	n-type region (P doped) 40 bilayers	Intrinsic region (SRO:SiO <sub>2</sub> =4.0nm :1.5nm ) 0 bilayers	p-type region (B doped)
Group#2 PIN2_0i PIN2_10i	n-type region (P doped) 40 bilayers SRO=4 nm	Intrinsic region (SRO:SiO <sub>2</sub> =4.0nm :1.5nm ) 0 bilayers 10 bilayers	p-type region (B doped) 25nm highly boron doped
Group#2 PIN2_0i PIN2_10i PIN2_20i	n-type region (P doped) 40 bilayers SRO=4 nm SiO2=1.5nm	Intrinsic region (SRO:SiO <sub>2</sub> =4.0nm :1.5nm ) 0 bilayers 10 bilayers 20 bilayers	p-type region (B doped) 25nm highly boron doped SRO

**Table 3.6**: The sample parameters of ncSi based diode devices.

The device fabrication starts from the PECVD thin film deposition of n-type and intrinsic bilayers and then the 25nm boron doped SRO monolayer. The boron and the phosphorus impurities were in-situ doped during SRO deposition by using 0.6 mol% Trimethylborane [TMB,  $B(CH_3)_3$ ] diluted in H<sub>2</sub> and the 0.6 mol% PH<sub>4</sub> diluted in SiH<sub>4</sub> respectively. The Si richness in SRO was controlled by the SiH<sub>4</sub> to N<sub>2</sub>O gas flow ratio with the consideration of maximum doping concentrations and low resistivity. Therefore, SiH<sub>4</sub> (PH<sub>4</sub>):N<sub>2</sub>O=6:5 was used for the P doped SRO and

SiH<sub>4</sub>:N<sub>2</sub>O:TMB=12:5:10 was used for B doped SRO. SiH<sub>4</sub>:N<sub>2</sub>O=6:5 was used for intrinsic SRO, which is consistent with P doped SRO. To protect the films in thermal annealing, a 20nm SiO<sub>2</sub> capping layer was deposited on top. After deposition, the samples were thermally annealed in a furnace at 1100 °C in a N<sub>2</sub> ambient for 1 hour to form ncSi, followed by etching of the capping SiO<sub>2</sub> in a 1:10 HF solution for 45s. Immediately after the removal of the capping oxide, 100nm Al was thermally evaporated. The Al film was patterned using photolithography and wet etching using H<sub>3</sub>PO<sub>4</sub> at 65 °C. With the Al pattern as the etching mask to protect the diode mesa, the top B doped layer and the intrinsic layers were selectively etched using CF<sub>4</sub>:O<sub>2</sub>=9 sccm: 4 sccm reactive ion etching (RIE) to reach the buried P doped n-type layer. Then the Al contacts were deposited on the exposed P doped bilayers by Al evaporation with the patterning and lift-off process. In order to form ohmic metal contacts, the samples were annealed in forming gas (4%H<sub>2</sub>/96%Ar) at 400 °C for 30mins. The final diode front contact structure consisted of eleven mesas (0.125mm x 1.0 mm<sup>2</sup> per mesa) and the contact pad (0.6 x 1.7 mm<sup>2</sup>) with a total area of 0.024 cm<sup>2</sup>. The distance (W<sub>a</sub> in Figure 3.16) between the interdigitated contacts on the exposed P doped layer and edge of the diode mesa was defined as 10µm. However, only the devices of PIN1 0i, PIN1 20i and PIN2 0i were successfully fabricated and the other devices with intrinsic bilayers failed due to over-etching in the RIE process, which will be discussed later.
#### 3.5.2. Measured I-V Characteristics

The measured dark I-V results of PIN1\_0i, PIN1\_20i and PIN2\_0i are shown in Figure 3.17 (a), (c) and (e). Diode behaviour in all the devices can be clearly observed. These devices have high series resistance as shown in Table.7, which can be calculated from dV/dI at voltage 0.8V - 1.0V. The large value of series resistance is primarily due to the lateral current flow in the highly resistive P-doped bottom layer. The low shunt resistance can be related to the relatively high non-linear leakage currents under reverse bias. The value of shunt resistance can be estimated from the slope of the I-V curves in the range of 0 V to 0.1 V.

One possible reason for the shunt conduction path is microscopic pinholes formed in the device layer during HF etching of the oxide capping layer. Therefore, these shunting paths in the structure of Al/ncSi(i)/ncSi(n)/Al or Al/ncSi(n) /Al will induce a non-linear leakage current originating from the space charge limited current. [112, 113] Similar shunting behaviour has already been reported in aSi:H *p-i-n* solar cell devices. The large amount of defects in the ncSi material can also contribute to the formation of conduction paths across the junction causing the shunting problem. [114]

Sample	PIN1_0i	PIN1_20i	PIN2_0i
R series ( $\Omega \cdot cm^2$ )	2.40 x10 <sup>+4</sup>	3.12x10 <sup>+3</sup>	2.64 X10 <sup>+2</sup>
$R_{shunt}(\Omega \cdot cm^2)$	6.72 x 10 <sup>+5</sup>	7.20 x 10 <sup>+5</sup>	1.70 x10 <sup>+5</sup>
V <sub>oc</sub> (mV)	230	205	210
$I_{sc}$ ( $\mu A/cm^2$ )	1.5	0.7	50

**Table 3.7:** The shunt resistance and series resistance extracted from the slope of IV curves. The  $V_{oc}$  and  $I_{sc}$  are from the illuminated IV curves.

The illuminated I-V results of the same devices are shown in Figure 3.17 (b), (d) and (f). These ncSi based devices exhibit poor photovoltaic performances similar to the other PV devices using nano-materials reported previously. [19, 115, 116] The open circuit voltage ( $V_{oc}$ ) at 205mV, 230mV and 210mV are achieved at 25 °C under 1-Sun illumination (100 mW/cm<sup>2</sup>), but the short circuit currents ( $I_{sc}$ ) are extremely low, with the best result of 0.043 mA/cm<sup>2</sup> for the device using 4nm SRO and no intrinsic bilayers. The non-steep slopes of I-V curves seen in the illuminated I-V results, indicate that the short circuit current ( $I_{sc}$ ) is strongly limited by the large series resistance. The estimated fill factors are only 24% -32%, which further confirm the inferior series resistance and shunt resistance in the devices.



**Figure 3.17:** Dark IV and Light IV results of ncSi based photovoltaic devices fabricated by PECVD deposition. (a) and (b) PIN1\_20i with 3.5nm SRO and 20 intrinsic bilayers. (c) and (d) PIN1\_0i with 3.5nm SRO and no intrinsic bilayers. (e) and (f) PIN2\_0i with 4nm SRO and no intrinsic bilayers

It is clear that the extremely low short circuit current ( $I_{sc}$ ) totally prevent the devices working as good solar cells. Although the high series resistance limits the extractable current, it notes that the poor material quality such as the low minority carrier lifetime and the low carrier mobility might be the more detrimental factors limiting the photovoltaic performance. This can be confirmed by the extraction of low photogenerated current ( $I_{ph}$ ), which represents the maximum current extractable regardless  $R_s$  and  $R_{SH}$ . It should be noted that the measured short circuit current ( $I_{sc}$ ) at V=0V bias can be much less than the real photogenerated current ( $I_{ph}$ ) if there is a considerable high series resistance as shown in Equation 3.5 and 3.6. This can be simply described by the single junction solar cell equivalent circuit in Figure 3.18.



Figure 3.18: The typical single junction solar cell equivalent circuit

$$I = I_o \left( exp \left[ \frac{q(V - IR_S)}{nkT} \right] - 1 \right) - \frac{(V - IR_S)}{R_{SH}} - I_{ph}$$
(3.5)

At V=0V external bias, the photocurrent (I<sub>ph</sub>) can be expressed as

$$I_{ph} = I_{sc} + I' \tag{3.6}$$

, where 
$$I' = I_o \left( exp \left[ \frac{q(I_{sc}R_S)}{nkT} \right] - 1 \right) + \frac{(I_{sc}R_S)}{R_{SH}}$$

From Equation 3.5, in order to extract  $I_{ph}$  directly from the illuminated I-V curve with high series resistance, a large enough negative bias would work. However, it is still impossible in practice to extract  $I_{ph}$  at negative voltage due to the leakage current from the poor shunt resistance as shown in Figure 3.17 (a, c, e).

Therefore, a rough estimation of  $I_{ph}$  calculated from Equation 3.6, if  $I' = I_o \left( exp \left[ \frac{q(I_{sc}R_S)}{nkT} \right] - 1 \right) + \frac{(I_{sc}R_S)}{R_{SH}}$  can be evaluated.



**Figure 3.19:** The series resistance effect on the I-V characteristics of PIN1\_0i device. The red dot line is the IV results after series resistance removal.

By knowing the series resistance from Table 3.7, the series resistance ( $R_s$ ) in the dark I-V of PIN1\_0i can be removed to get Equation 3.7 and the corrected IV is shown in Figure 3.19.

$$I = I_o \left( exp \left[ \frac{q(V)}{nkT} \right] - 1 \right) - \frac{V}{R_{SH}}$$

$$(3.7)$$

Therefore, I' can be estimated in Figure 3.19 by finding  $V=I_sR_s$  in the non- $R_s$ -corrected curve in Figure 3.19.

It is noticeable that the I-V diode characteristic will not be limited by  $R_s$  up to 0.5-0.6 V. The products of  $I_{sc}$  and  $R_s$  shown in Table 3.7 are only 36mV, 3mV and 12mV, which are much lower than 0.5 V (500 mV). Therefore, the calculated photogenerated currents ( $I_{ph}$ =Isc + I') are extremely low and there only has a very small effect in reducing the short circuit currents ( $I_{sc}$ ). This result suggests that the high series resistance may not the only major reason for poor photovoltaic performance. Other factors likely to cause this poor performance could be the very low effective minority carrier lifetime and the low carrier mobility of the ncSi material.

The low open circuit voltage results are also consistent with low effective minority carrier lifetime. The open circuit voltage ( $V_{oc}$ ) reflects the degree of splitting of electron and hole quasi-fermi levels, which is determined by the material bandgap and the excess minority carrier density generated under illumination. The ncSi materials with larger bandgap, as indicated by the high PL peak (1.3 eV -1.4 eV) in Figure 3.20,

are expected to show higher  $V_{oc}$ . However, this quasi-fermi level splitting can be more strongly suppressed by the recombination due to defects that limit the excess minority carrier generation. The suppression effects due to defects and recombination outweigh the increased bandgap in ncSi based diode devices in determining the V<sub>oc</sub>.



Figure 3.20: Photoluminescence results of PIN1 devices.

One very possible reason for the extremely low lifetime could be the high doping density generally used to form p-type and n-type ncSi. Although it has been reported that phosphorus and boron dopants can passivate the ncSi interface defects at low doping density, [23, 39] much higher doping density is generally used in order to achieve the acceptable conductivity. This can be mainly attributed to the low B/P doping efficiency in ncSi from the self-purification mechanism. [117] Therefore, a large number of excess dopant atoms aggregate at ncSi interfaces and act as

recombination defects rather than effective doping. Further study should be done to increase the effective doping in ncSi.

### **3.5.3.** Further Device Process Development

As shown in Figure 3.17, only the devices of PIN1\_0i, PIN1\_20i and PIN2\_0i were successfully fabricated but the other devices with intrinsic bilayers all failed because they were open circuit. This could be due to the failure to form a good Al contact on the phosphorous doped bottom layer after reactive ion etching (RIE). The failed samples were investigated by Scanning Electron Microscopy (SEM). As the crosssectional SEM in Figure 3.21 indicates, there is an 80-100nm rough surface clearly identifiable. One possible explanation for the contact failure is that CF4:O<sub>2</sub> RIE selectively etches Si faster than SiO<sub>2</sub> in annealed SRO layers, leaving a thick and more SiO<sub>2</sub>-like rough surface above the remaining P-doped bottom layer. As a result, this insulating layer can completely block current conduction. This selective etching effect becomes more detrimental while etching thicker SRO layers, as the intrinsic bilayers are present.



Figure 3.21: The cross-section SEM image of the RIE etched annealed ncSi thin film.

The  $O_2$  addition in RIE helps to maintain a stable etching rate by suppressing polymer formation. However, it should be noted that the addition of  $O_2$  can strongly increase the Si etching rate compared to the SiO<sub>2</sub> etching rate, due to the formation of SiO<sub>2</sub> during the etching process. [118] Furthermore, the complex local environment depending on excess Si (Si%) in the annealed SRO material may further complicate the RIE Si/SiO<sub>2</sub> selectivity, which is very different from etching bulk Si and SiO<sub>2</sub>. Therefore, it is difficult to control RIE to uniformly etch the annealed SRO layer by using CF<sub>4</sub>:O<sub>2</sub>. Adding H<sub>2</sub> and CHF<sub>3</sub> or etching at low pressure may help to achieve anisotropic and less chemically selective RIE etching. [119]

Rather than tediously calibrating the RIE etching parameters for uniform SRO etching and suffering unstable SRO etching, a lift-off device fabrication method is proposed to potentially bypass the RIE process for thin film ncSi based junction device fabrication. The process is illustrated in Figure 3.22. Negative nLOF2020 photoresist was used to make a diode device pattern on n-type bilayers followed by the deposition of the intrinsic and p-type layers. Before the deposition process, the surface of the ntype layer was cleaned using a  $O_2$  plasma for 15mins and an HF dip carried out to remove the protective SiO<sub>2</sub> capping. The bottom n-type layer was exposed by lifting off the nLOF2020, i-layer and p-type layer in NMP (1-Methyl-2-Pyrrolidone) as shown in Figure.21 (c) and (d). In order to avoid Al contact flagging after metallization, the bi-layer lift-off resist process (LOR [120] and S1818) was developed in Figure.21 (e-i). The undercut depth in LOR resist depends on the softbaking time, temperature and developing time and a 2 µm -5 µm undercut can be controlled. This lift-off process has been successfully applied for p-i-n ncSi based photovoltaic devices fabrication. [116]



Figure 3.22: Lift-off process using double layer PR to avoid reactive ion etching.

#### 3.6. Conclusion

In the first section of this chapter, plasma enhanced chemical vapour deposition (PECVD) has been investigated for the fabrication of ncSi embedded in SiO<sub>2</sub> and boron/phosphorus doping in ncSi. By optimizing the PECVD process parameters, the stoichiometry of SRO can be controlled. Low SiO<sub>2</sub> and SRO deposition rate can be achieved at about 6nm/min and 10nm/min, respectively, which is low enough for superlattice structure fabrication.

The detailed chemical composition of SRO before and after thermal annealing has been investigated by XPS and FTIR. The incorporation of large amounts of nitrogen and hydrogen in SRO has been identified. The nitrogen will not only change the ncSi crystal formation process during annealing, but it will also influence the electrical properties of ncSi. Although the hydrogen in SRO by PECVD benefits the material quality for defect passivation, the high temperature annealing causes strong hydrogen effusion. The ncSi materials after annealing exhibit more defects, which have been identified from the increased refractive index and optical absorption due to hydrogen effusion.

The boron and phosphorus doping in ncSi can dramatically reduce the resistivity by *in-situ* doping and diffusion doping methods. For in-situ doping in ncSi, the phosphorous doped ncSi show much lower resistivity than boron doped ncSi. By analysing the effects of silicon content and doping concentration on resistivity, it is evident that phosphorous can enhance the silicon crystallization but not boron. After the demonstration of ncSi preparation and doping by PECVD, the ncSi based single junction photovoltaic devices are fabricated and analysed. The detailed fabrication process and device characterization results are presented in the second part of this chapter.

The diode I-V characteristics and the best open-circuit voltage of 230mV have been achieved. However, the diode devices exhibit extremely low short-circuit current preventing the devices working as proper solar cells. The parameters extracted from electrical measurements indicate that the photovoltaic performance is limited by the low current transport from high sheet resistance and the strong non-radiative recombination from high doping concentration. These limiting factors can be attributed to the ineffective doping (low doping efficiency) in ncSi, which is a general problem for nano-semiconductor materials. Further research of ncSi doping and carrier transport is of great significance for improving the electrical properties of ncSi and achieving the 3<sup>rd</sup> generation all silicon tandem solar cell.

## **Chapter 4**

# Electrically Active Boron Doping in Nanocrystal Silicon by Capacitance-Voltage Characterization

**This chapter is based on the publication**: Zhang, T., Puthen-Veettil, B., Wu, L., Jia, X., Lin, Z., Yang, T.C.-J., Conibeer, G., and Perez-Wurfl, I.: 'Determination of active doping in highly resistive boron doped silicon nanocrystals embedded in SiO<sub>2</sub> by capacitance voltage measurement on inverted metal oxide semiconductor structure', J. Appl. Phys., 2015, 118, (15), pp. 154305

**Overview:** In this chapter, we mainly address the challenge of electrical characterization of active boron doping in nanocrystal silicon by using capacitance-voltage (CV) measurement. The inverted metal-oxide-semiconductor (MOS) devices in vertical structure circumvent parasitic parameters of large sheet resistance and edge effects, making accurate CV measurements and curve fittings possible to investigate the electorally active doping concentration, carrier transport dynamics and defects effect in nanocrystal silicon. By studying capacitance-voltage characteristics as well as resistivity, XRD and photoluminescence (PL) spectra, we elucidate the role of heavily doping to the electrical properties of boron doped ncSi and realize the importance of improving doping efficiency.

#### 4.1. Introduction

Doping nanocrystal silicon (ncSi) is of great interest for the development of ncSi based photovoltaic and photonic devices. In the previous decades, many investigations have been undertaken to understand the boron and phosphorus doping in ncS and the corresponding carrier transport mechanisms in this nanostructured materials. The dopant atomic concentration can be accurately measured by secondary ion mass spectrometry (SIMS) and three-dimensional atom probe tomography (APT) provides an atomic scale picture of their spatial distribution. However accurate this techniques can be to quantify dopant density and distribution, the results cannot determine the electrically active dopants. The difficulty arises from the large amount of dopant atoms that exist in the dielectric matrix and the interface regions, where the dopant atoms may be electrically inactive. Also, the activation of a dopant is not guaranteed even if it is found insider the nanocrystal. Although phosphorous doping inside ncSi has been clearly identified from the hyperfine splitting doublet centred at g=1.998 by electron paramagnetic resonance, [23, 121] in fact, there is still a lack of direct electrical characterization methods to quantitatively evaluate the electrical properties of doped ncSi thin films due to the high resistivity, especially for boron. The high resistivity results in an extremely high sheet resistance that complicates the electrical measurements so the most commonly used techniques such as four point probe and Hall measurements are generally not applicable. Therefore,

modifications and development of new electrical measurement techniques as well as novel device designs are necessary.

Capacitance-Voltage (CV) characterization is a quick and accurate method to investigate the electrical properties of semiconductor materials and devices. For ncSi, this technique is more generally used to explore the charging/discharging hysteresis behaviour in single-/multi-layer or ultra-thin ncSi material, [122-124] but rarely used for the evaluation of ncSi doping. The only reported attempt of using CV measurement to determine the electrical properties of B/P doped ncSi, such as doping concentration, doping type and interface traps density, was carried out by Lin et al. using a lateral metal oxide semiconductor (MOS) structure on quartz substrates as shown in Figure 4.1 (a). [125] However, in that study, only high Si content ncSi films with a resistivity of about 0.72  $\Omega$ ·cm were measured. Samples with low Si content or lower doping (with a resistivity of 100  $\Omega$  cm or more) were not measurable due to the corresponding M $\Omega$ /  $\Box$  sheet resistance. This large sheet resistance complicated the device analysis due to the distributed parasitic resistance and capacitance network that needed to be taken into account (Figure 4.1 (a)). This in turn made it difficult to interpret the measured CV results. Additionally, in lateral MOS structure, the gate capacitance is proportional to the gate radius rather than the gate area due to the current crowding effect. This effect causes frequency dispersion in the CV results, which complicated evaluating the carrier dynamic characteristics in ncSi. Here we demonstrate that using an MOS

device in a vertical structure circumvents problems accompanying the large sheet resistance and permits the characterisation of doped ncSi with high resistivity.

This chapter describes the work done to achieve reliable CV measurements for characterising doped ncSi. In particular, we characterize boron doped ncSi samples, which could not be measured using the lateral MOS CV or Hall techniques. We show that an inverted ncSi MOS device can be used to avoid the complications arising from lateral current flow. The schematic MOS device in an inverted structure by using a p++ Si substrate as the conductive contact is shown in Figure 4.1 (b). We will demonstrate that ncSi films with higher resistivity (200-400  $\Omega$ ·cm) can be measured. The ncSi thin films with various boron doping densities have been prepared and characterised to study the applicability of this CV structure. To analyse the measured data, high frequency CV modelling has been undertaken to include the effects of doping concentration, interface trap density and flat band voltage. Materials with high Si% and low B doping have been also tested by CV for further understanding of ncSi doping and carrier transport.

#### 4.2. The Inverted MOS Devices



#### 4.2.1. Sample preparation

Figure 4.1: (a) The lateral MOS device. (b) The inverted MOS device

The fabrication of the inverted MOS in a vertical structure started with a dry thermal oxidation of a p++ Si wafer (Boron, 0.001-0.005  $\Omega$ ·cm) at a temperature of 1000°C to form an SiO<sub>2</sub> layer of about 50nm. The relatively thick oxide was used to avoid high leakage current which could occur from boron diffusion from the highly doped ncSi layers deposited on top of this oxide. Before loading in the sputtering chamber for the next step in the fabrication, the actual thickness of the thermal SiO<sub>2</sub> thickness was confirmed by ellipsometer to be 43-46 nm. On top of the oxide, we deposited a superlattice structure consisting of 30 bilayers of 1.8nm SiO<sub>2</sub> and 4nm silicon rich oxide (SRO) in an AJA ATC-2200 sputtering system. Before sputtering deposition, Piranha cleaning (H<sub>2</sub>SO<sub>4</sub>:DI Water=1:1 for 10mins) was used to remove surface contaminants followed by 1% highly diluted HF dip with very low etching rate for 5 seconds to further clean the surface. This 1% HF

solution was diluted from 1:10 HF solution to 1:100 to only remove 1-3 nm of the oxide surface without causing pin holes that could shunt the capacitor.

The intended SRO composition was SiO<sub>0.66</sub>, corresponding to a Si/SiO<sub>2</sub> volume ratio of 11:9. Boron (B) dopants were co-sputtered during the SRO film deposition. Three different power levels (5 W, 10 W and 15 W) were applied to the boron target to obtain different boron concentrations. The Si/SiO<sub>2</sub> ratio and the thickness were kept constant for the various B concentrations. Finally, a 25 nm SiO<sub>2</sub> capping oxide was deposited to protect the superlattice in the subsequent high temperature annealing. To maintain the quality of the thermal SiO<sub>2</sub> between the superlattice and the Si substrate, the samples were annealed at a temperature of 1050 °C for 2 hours, only 50°C higher than the thermal oxidation temperature.

Aluminium (Al) was selected for the front and back metal contacts. The front SiO<sub>2</sub> capping and the native oxide on the backside of the Si substrate were carefully removed using 7:1 BOE etching respectively before Al deposition. The front 200nm Al gate contact was patterned by photolithography and wet etching using H<sub>3</sub>PO<sub>4</sub>: deionized water=1:1 at 65 °C. As shown in Figure 4.2, the round CV gate contacts were patterned in three different diameter sizes of 1000  $\mu$ m, 500  $\mu$ m and 250  $\mu$ m. The TLM contact patterns were formed to evaluate resistivity. There were 8-10 groups of MOS and TLM devise fabricated for each boron doping level. Reactive ion etching using CF4:O<sub>2</sub> was applied to isolate the MOS device with Al as the etching mask. To reserve devices and protect TLM patterns, 4-5 groups of devices and TLM patterns were masked during RIE etching. The etching depth

was controlled between 190-220 nm to ensure the removal of the superlattice (170nm - 180nm).



**Figure 4.2:** The photolithography mask for Al metallization patterning. The right pattern is the circular TLM next to the MOS devices on the left.

Finally, in order to promote the formation of Al ohmic contacts and hydrogen passivation, the devices were annealed at 450°C for 30 mins in a forming gas (4%  $H_2 / 96\%$  Ar) ambient. The final device structure is schematically shown in Figure 4.1 (b).

#### 4.2.2. Advantages of The Inverted MOS Structure

The main advantage of using the inverted MOS in a vertical device structure is to circumvent the large sheet resistance. In order to achive the vertical structure, a highly doped p-type Si substrate has been used to work as the conductive gate. The most significant reason of using p++ wafer is that the wafer maintains its high conductivity even after the high temperature annealing process. The doping concentration of p++ wafer is over  $5 \times 10^{19}$  cm<sup>-3</sup> with a resistivity of 0.001  $\Omega$ .cm. Therefore, the capacitance due to the p++ substrate is much larger than that of the thick oxide and the space charge region in the doped ncSi superlattice layer. As the capacitors are connected in series, the large capacitance due to the substrate can be neglected.

In the lateral structure as shown in Figure 4.1 (a), the large sheet resistance and the distributed circuit elements cause edge effects so that the measured capacitance is proportional to the perimeter rather than the gate area. For the inverted MOS device (Figure 4.1 (b)), the linear relationship between the capacitance and the gate area can be confirmed as shown in Figure 4.3. It is a good indication that the edge effect is negligible. By comparing the capacitance before and after forming gas annealing in Figure 4.3, the lower capacitance before forming gas annealing (FGA) can possibly be due to the capacitance resulting from Schottky contacts. This also gives rise to frequency dispersion effects that will be discussed later in this chapter.



**Figure 4.3:** The capacitance is only linearly proportional to the gate area, which indicates that there is no edge effect in the inverted MOS device. The frequency and the gate bias voltage ( $V_b$ ) also do not change the linear relationship. FGA means forming gas annealing.



**Figure 4.4:** (a) The I-V results by TLM measurement showing the contact is ohmic. (b) The TLM plot (resistance vs. ln(Rout/Rin)) for the calculation of sheet resistivity and the contact resistance. The sample shown here is boron doped ncSi with 5W sputtering power.

The Al contact can be another critical parasitic element, which can contribute to an additional capacitance in the CV measurement if a Schottky contact is formed rather than an ohmic one. However, the forming gas annealing ensures that a Schottky contact is not formed. From the I-V results of Circular-TLM measurements as shown in Figure 4.4, the linear I-V results (a) and TLM plot (b) confirm the formation of ohmic contacts after forming gas annealing. Therefore, there is no need to consider the parasitic capacitance from the contact in the CV modelling.

#### **Boron Power 15W Boron Power 10W Boron Power 5W** Counts (au.) (220)(311) 2theta (degree)

#### 4.3. Structural characterization using XRD

**Figure 4.5:** The GIXRD results show the characteristic Si XRD peaks, which confirm the existence of ncSi. The calculated ncSi feature sizes are 3.2 nm, 4.5 nm and 4.8 nm for boron sputtering power of 5 W, 10 W and 15 W respectively. It shows that boron impurity can enhance the Si crystallization.

Figure 4.5 shows the GIXRD results of  $SiO_{0.66}$  with various boron doping. The three broad peaks are evident at 28.4°, 47.4°, 56.3°, representing the formation of

Si nanocrystals. The average ncSi size can be estimated by Scherrer's equation. The approximated average ncSi crystal sizes are 3.2 nm, 4.5 nm and 4.8 nm. It is identified that higher boron impurity concentration enhances the ncSi formation in hight temperature annealing, which is different from the results reported by Hao et al.. [34] The mechanism of impurity induced enhancement or supression on the nanocrystal growth is still not well understood, especially for boron. As the doped ncSi samples with different doping concentrations have the identical silicon content (Si%), the smaller crystal size indicates the larger amorphous shell, which should cause lower carrier transport (mobility).

#### 4.4. Photoluminescence characterization

Figure 4.6 shows the photoluminescence (PL) results of the B doped ncSi after forming gas annealing. The photoemission peaks shown in the photoluminescence (PL) spectra of boron doped ncSi confirm the existance of PL active nanocrystals and the higher emission energy indicate the persistence of silicon quantum confinement effects. The photoluminescence (PL) was measured at room temperature by a ¼ meter monochromator (CornerstoneTM 260i) equipped with a silicon CCD camera at -30 °C using a 10 seconds integration time. The excitation source is a 50 mW solid state 405 nm (blue) CW laser source with a spot size of 0.5 mm diameter. The PL spectra were corrected for the spectral response of the system.



**Figure 4.6:** (a) PL spectra measured from the intrinsic ncSi and boron doped ncSi. (b) The normalized PL results. The normalized PL spectra of ncSi doped with boron power 10W and 15W are identical.

In Figure 4.6 (b), an asymmetric broad PL peak can be clarely observed with maxima within the range 1.35 eV - 1.4 eV. The PL intensity quenches with increasing boron doping concentration, in agreement with previous reports indicating successful boron doping. [126, 127] This PL quenching with increased boron concentration can be mainly attributed to two reasons:

1) An increase in the non-radiative Auger recombination by successful B doping in ncSi. [128]

2) An increase in the non-radiative recombination from defects at ncSi interfaces.[20, 39]

Because of the effect of dopants in quenching the PL signal, the PL signal observed is due to emission originating in the undoped ncSi with well passivated surfaces. We propose that larger ncSi tend to incorporate dopants and become PL inactive. However, there are still smaller ncSi [42] remaining intrinsic and PL active, even at high doping concentration. The PL spectra should be mainly from these undoped small ncSi. From Figure 4.6 (b), this can be further confirmed by the 50 meV PL peak blue-shift and the broader PL spectra at higher emission energy.

The self-purification effect describes the difficulty in doping small ncSi due to the high doping formation energy. [129] The formation energy is inversely proportional to ncSi size [28] so that the stronger self-purification in smaller ncSi tends to keep them undoped and luminescent. Experimentally, the XPS results by Hao et al. also concluded the low possibility of boron incorporation from the absence of B-B/B-Si bonding in small ncSi from SRO with very high O/Si ratio. [127] From Figure 4.6, by further increasing the boron doping density using 10 W and 15 W on the Boron target, there is no PL peak shift but only a decrease in the intensity. This is further consistent with the excess boron causing an increase in non-radiative defects which further quenches the PL signal.

#### 4.5. CV Measurement Results and Discussions

#### 4.5.1. CV characteristics of boron doped ncSi MOS

Capacitance-Voltage (CV) measurements were carried out using an HP4284A impedance analyser. A sweeping DC gate voltage (Vg) was applied to modulate the surface space charge region of the ncSi layer and a small (0.5 V pp) AC signal was used to measure the device impedance. It is important to note that, due to the inverted MOS structure, the positive electrode is connected to the p++ substrate rather than the top Al contact (Figure 4.1 (b)) during CV measurement. The measured impedance Z was interpreted as a series connection of a capacitor and a resistor (Cs-Rs) such that  $Z=Rs-j(\omega Cs)^{-1}$ . The gate voltage range was ±25 V with a 0.2 V step size. The sweep delay time was set between 500 ms and 1 s in order to ensure the measurement was in an equilibrium condition at each gate bias voltage. The CV results of boron doped ncSi (SiO<sub>0.66</sub>) at different doping levels are summarized in Figure 4.8 (a), (b) and (c).

The characteristic CV curves exhibit the transition from accumulation under negative DC bias to inversion under positive DC bias, which is consistent with a characteristic MOS CV curve on a p-type silicon. [130] Therefore, it directly confirms that the ncSi are p-type doped. The slight capacitance decrease at negative bias (in accumulation) is due to the depletion of the p++ Si substrate  $(C_{p++})$ . At positive DC bias, the measured capacitance only consists of the oxide capacitance ( $C_{ox}$ ) and the depletion or inversion capacitance from the ncSi layer  $(C_{ncSi})$  because the p++ wafer only contributes a negligible large accumulation capacitance connected in series.



Figure 4.7: Equivalent circuit of MOS in accumulation and inversion conditions

The rising capacitance curves in the 10 V to 25 V gate bias range is akin to what would be observed in the case of strong inversion. This is probably a false strong inversion due to the strong carrier generation/recombination by defects/traps at the SiO<sub>2</sub> interface. The false inversion has also been observed in HfO<sub>2</sub> gate or Al<sub>2</sub>O<sub>3</sub> gate MOS devices with high interface traps/defects. [131, 132]

Another important feature shown in Figure 4.8 (a-c) is the frequency dispersion. The CV curves shifts to lower values at higher AC frequency, which is similar to the results from the lateral MOS devices. [125] In the lower frequency regime, the accumulation capacitance at negative bias approaches that expected for the measured 45 nm oxide capacitance (about 602 pF). To model this frequency dispersion, a frequency dependent effective oxide capacitance is introduced in the model,  $(C_{ox\_eff(f)})$ , in series with the ideal MOS structure, as shown in Figure 4.7 (c) and Figure 4.8. With this model, one can remove the dispersive element from the measured capacitance data ( $C_{data}$ ) with a simple equation. The corrected capacitance ( $C_{norm}$ ) can be calculated by

$$C_{\text{norm}} = \frac{1}{\frac{1}{C_{\text{data}}} - \frac{1}{C_{\text{ox_eff}}} + \frac{d_{\text{ox}}}{\varepsilon_0 \varepsilon_{\text{ox}} \cdot A}}$$
(4.1)

, where A is the Al front contact area. The SiO<sub>2</sub> thickness ( $d_{ox}$ ) can be measured by Ellipsometry before the ncSi deposition.  $C_{ox\_eff(f)}$  has been determined from the maximum value in the accumulation regime because at this bias condition no depletion capacitance forms in the ncSi layer and only the oxide capacitance dominates the total device impedance.



**Figure 4.8:** CV results of boron doped ncSi with various doping power (a) B5W, (b) B10W, (c) B15W. The CV curves shift down with higher frequency. The corrected CV results (d, e, f) without frequency dispersion.

After removing the frequency dependent  $C_{ox\_eff(f)}$  from the measured capacitance, the corrected results are shown in Figure 4.8 (d-f). It can be seen that the CV curves at different frequency coincide well with each other in both the accumulation and the depletion bias regimes. The coincidence of corrected CV curves demonstrates that the effective  $C_{ox\ eff(f)}$  should be the only frequency dependent element.

### 4.5.2. CV frequency dispersion

The typical reasons causing the additional parasitic capacitance (like  $C_{lossy}$  or  $C_m$ ) in the MOS device, such as edge effect and oxide leakage, can be ruled out for our samples. As discussed in 4.2.2, the vertical device structure can effectively avoid the effect of the large sheet resistance responsible for the edge effects (Figure 4.1 (a)). Additionally, from a direct I-V measurement, the low current density of about 100 nA/cm<sup>2</sup> at 1V bias for 43 nm~46 nm oxide means the oxide resistivity is in the order of  $10^{12} \Omega$ .cm, which confirms that the oxide is not particularly leaky.

By comparing the CV curves of 5W boron doped sample before (Figure 4.8 (a)) and after (Figure 4.9(a)) forming gas annealing, the frequency dispersion at maximum capacitance in the accumulation regime reduces from 16% /decade to 5% /decade over the frequency range from 10 kHz to 1 MHz. The disappearance of the CV curve stretch, as compared between Figure 4.8 (d) and Figure 4.9 (b), can be mainly attributed to the passivation of interface traps and improved contacts after FGA. These results suggest that the frequency dispersion effect in our MOS device is related to the defects/traps at the gate interface region or in ncSi.



**Figure 4.9:** (a) The CV results of boron power 5W before forming gas annealing. (b) The corrected CV results. The stronger frequency dispersion and the CV curve stretch are obvious, comparing to samples after forming gas annealing (Figure 4.8 (a)).

Firstly, it has been reported that carrier tunnelling into near-interface defects and border traps in the dielectric layer will cause CV frequency dispersion in Al<sub>2</sub>O<sub>3</sub>/AlGaAs MOS devices and a more abrupt interface could reduce the CV frequency dispersion effect, [133] which is similar to our case. In the case of our samples, besides the typical interface traps at the ncSi film surface, a thin lossy SiO<sub>x</sub>:B dielectric layer is formed between the thermal SiO<sub>2</sub> and the ncSi film and defects/traps in the lossy dielectric layer is represented by the additional parasitic capacitance in series with the ideal MOS structure as shown in Figure 4.7 (c). By forming gas annealing, hydrogen (H) is able to passivate the defects/traps in the lossy dielectric layer so as to reduce the frequency dispersion.



Figure 4.10: The schematic of displaced charges causing the frequency dispersion.

The second possible reason of the frequency dispersion could be the extremely low carrier mobility in ncSi. [134] In CV measurement, the small signal capacitance is defined as  $C=\Delta Q/\Delta V$ , where  $\Delta Q$  is the charge increment by the voltage increase  $\Delta V$ . At higher frequency, the majority carriers with low mobility cannot follow the AC signal to contribute to the space charge increment ( $\Delta Q$ ) near the ncSi surface region, thus part of the space charge increment comes from displaced free carriers from more distanced locations (d') [135] as shown in Figure 4.10. The displaced charges increase the effective space charge region width, and hence the measured capacitance  $C_{data}$  will be smaller ( $C=\varepsilon/d$ ). The passivation of defects/carrier traps will increase the carrier mobility and also reduce the d'. Therefore, the carrier dynamic response to the AC signal increases and shows weaker dispersion.

#### 4.5.3. Capacitance Voltage Modelling

Similar to the classical Si MOS, the capacitance from the doped ncSi can be modelled by numerically solving Poisson's equation and the corresponding charge and the potential balance equations. [136] The model starts from numerically solving Poisson's equation with the boundary condition of surface potential  $\Phi_s$ .

$$\frac{\partial^2 \Phi_{(x)}}{\partial x^2} = -\frac{q \left[ p_{(x)} + N_d^+ - n_{(x)} - N_a^- \right]}{\epsilon_0 \epsilon_s}$$
(4.2)

, where,  $N_d$  and  $N_a$  are donor and acceptor concentrations. The electron and the hole carrier concentrations are  $n_{(x)}$  and  $p_{(x)}$  and  $\varepsilon_s$  is the permittivity. For each given surface potential ( $\Phi_s$ ), the spatial profiles of the carrier density and potential in the space charge region can be obtained. The net space charge ( $Q_{ncSi}$ ) in the ncSi layer can be calculated by

$$Q_{ncSi}(\Phi_s) = \int q(p_{(x,\phi s)} + N_d^+ - n_{(x,\phi s)} - N_a^-) dx$$
(4.3)

Using a small surface potential fluctuation  $\Delta \Phi_s$  as the AC signal, the semiconductor capacitance  $C_{ncSi}$  can be written as

$$C_{ncSi} = \frac{\Delta Q_{ncSi}(\Phi_s)}{\Delta \Phi_s} = \frac{q(\Delta p_{(x,\Delta \Phi s)} - \Delta n_{(x,\Delta \Phi s)})}{\Delta \Phi_s}$$
(4.4)

, where  $\Delta Q_{ncSi}$  is the change of net charge ( $Q_{ncSi}$ ) with the corresponding surface potential fluctuation  $\Delta \varphi_s$ . By using Equation 4.2 - 4.4, the low frequency capacitance can be calculated. The deep depletion situation can be modelled by eliminating the minority carrier charge term ( $p_{(x)}$  for n-type and  $n_{(x)}$  for p-type) in the Poisson's equation (Equation 4.2) because no inversion layer is generated. For high frequency situations (generally about 1 MHz or over), we modify the model by removing the minority carrier charge response to the AC signal (the terms of  $\Delta n_{(x, \Delta \Phi_s)}$  for p-type) in Equation 4.4 and it is assumed that no inversion charge redistribution effect occurs for the highly doped materials.

The measured capacitance  $(C_{tot})$  and the gate voltage  $(V_g)$  can be calculated from

$$\frac{1}{C_{tot}} = \frac{1}{C_{it} + C_{ncSi}} + \frac{1}{C_{P++}} + \frac{1}{C_{ox}}$$
(4.5)

$$V_{g} = \phi_{s} - V_{p++} + V_{fb} - \frac{Q_{it}(\phi s) + Q_{ncSi}(\phi s)}{C_{ox}}$$
(4.6)

where  $C_{ox}$  is the oxide capacitance,  $C_{it}$  is the capacitance due to the charged interface states.  $V_{P++}$  and  $C_{P++}$  are the voltage drop and capacitance from the p<sup>++</sup> Si wafer.  $V_{fb}$  is the flatband voltage.  $Q_{it}(\Phi s)$  is the charge from the charged interface traps. By knowing the oxide thickness from ellipsometry measurment, the oxide capacitance can be calculated by

$$C_{ox} = \frac{\varepsilon_0 \varepsilon_{ox} \cdot A}{d_{ox}}$$
(4.7)

With the charge balance equation, the voltage drop  $(V_{P^{++}})$  on the P++ wafer is estimated by

$$Q_{ncSi} + Q_{p++} + Q_{it} + Q_{fb} = 0$$
(4.8)

$$V_{P++} = -\frac{Q_{P++}^2}{2q\epsilon_s N_{p++}}$$
(4.9)

The CV results at high frequency (1 MHz or higher) have been used for fitting the measured data without considering the frequency dependent  $C_{it(f)}$  due to interface traps because the carrier transitions in interface traps cannot follow the AC signal at such high frequency. However, it should be noted that the charge  $Q_{it}$  due to interface traps under DC gate bias still contributes to an additional voltage drop (V= $Q_{it}/C_{ox}$ ) across the dielectric gate, which is the reason for the stretched CV curves at high frequency. The shift and stretch of CV curves can be modelled by taking into account the acceptor-type and donor-type interface states [136, 137] described as,

$$Q_{it(V_s)} = -q \int_{E_v}^{E_c} \left[ D_{ita(Et)} * F_{SA}(E_t - E_f) - D_{itd(Et)} * F_{SD}(E_t - E_f) \right]$$

$$* d E_t$$
(4.10)
$$F_{SD}(E_t) = \left[1 - \frac{1}{1 + g_D \exp[(E_F - E_t)/kT]}\right]$$
(4.11)

$$F_{SA}(E_t) = \frac{1}{1 + g_A \exp[(E_t - E_F)/kT]}$$
(4.12)

where  $D_{itd(Et)}$  and  $D_{ita(Et)}$  are the acceptor-type and donor-type trap states distribution in the band gap respectively. The ground-state degeneracy is adopted from silicon as  $g_{b}=2$  and  $g_{A}=4$  and  $E_{F}$  is the Fermi level.

In this model, we used a permittivity of 5.56, which was measured from the intrinsic SiO<sub>0.66</sub>. A sample made into a structure of Al/SRO<sub>0.66</sub>/SiO<sub>2</sub>/p++ Si was used for extracting this permittivity. As there are no carriers in intrinsic SiO<sub>0.66</sub>, the SiO<sub>0.66</sub> layer works as a capacitor in series with the SiO<sub>2</sub> layer. This was confirmed by the observation of a constant capacitance (C<sub>m</sub>) value for a DC sweep between  $\pm 3V$  for frequency from 50 kHz to 1MHz. The measured capacitance (C<sub>m</sub>) can be represented by  $1/C_m=1/C_{Si0.66}+1/C_{SiO2}$ . Therefore, the permittivity of intrinsic SiO<sub>0.66</sub> ( $\epsilon_{SiO0.66}$ ) can be calculated from

$$\varepsilon_{\rm SiO0.66} = \frac{d_{\rm SiO0.66}}{\left(\frac{A}{C_{\rm m}} - \frac{d_{\rm SiO2}}{\varepsilon_{\rm SiO2}}\right)} \tag{4.13}$$

, where  $d_{Si0.66}$  and  $d_{SiO2}$  are the layer thickness measured by ellipsometry and A is the gate area (cm<sup>2</sup>).

#### 4.6. Electrical Properties of Boron Doped Si Nanocrystals

By using the numerical simulation model, the CV results at high frequency (1 MHz) have been fitted to evaluate doping concentration, doping type, interface trap density and flat band voltage. No strong inversion or deep depletion effects were considered. The fitting results are shown in Figure 4.11 and Table 4.1. The ideal CV curves (green dashed lines) without fitting the interface traps are presented in order to show the strong effects from interface traps. Although it has been widely reported that the doping of ncSi is difficult, [23, 24, 32, 33, 129, 138] our results show that in-situ boron doping at high temperature is possible.



**Figure 4.11:** Fitting results of 1MHz high frequency CV curves for various boron densities. The green dashed lines represent the ideal CV curves without considering the interface traps (Dit). The red solid lines are the fitting results of the measured CV data (dot lines) with Dit considered.

The most significant effect observed is the high electrically active boron doping concentration, in the order of  $10^{18}$ - $10^{19}$  cm<sup>-3</sup>. By referring to our previous XPS and SIMS results, [19, 34] the atomic boron concentration should be in the range of  $5x10^{19}$ -  $5x10^{20}$  cm<sup>-3</sup> for the boron sputtering power used in this work. This leads to a low doping efficiency, approximately less than 5%. The majority of boron dopants should be still electrically inactive, which may behave as defects and carrier traps to further reduce the carrier mobility.

Although the doping efficiency seems relatively high compared to that of phosphorous doping in free standing ncSi [23] and ncSi fabricated by PECVD, [33] it does not mean that boron is a more effective dopant than phosphorous for doping ncSi. It is worth noting that we used relatively high silicon content in SRO (SiO<sub>0.66</sub>), so that the ncSi material should contain large ncSi, interconnected in a Si network and with smaller spacing between isolated ncSi [139]. The existence of this Si network will increase the dopant incorporation in "ncSi".

	SiO <sub>2</sub> thickness (nm)	Resistivity (TLM) (Ω.cm)	Doping (cm <sup>-3</sup> )	V <sub>fb</sub> (V)	Mobility <sup>a</sup> (cm <sup>2</sup> /V/s)
B5W	45.5±2	3.88x10 <sup>2</sup>	2.5x10 <sup>18</sup>	-2	6.44x10 <sup>-3</sup>
B10W	43.7±3	2.19x10 <sup>2</sup>	1.4x10 <sup>19</sup>	-1.3	2.04 x10 <sup>-3</sup>
B15W	42.9±5	3.34x10 <sup>2</sup>	1.0x10 <sup>19</sup>	-0.7	1.87 x10 <sup>-3</sup>

Table 4.1: Fitting results for boron doped ncSi

<sup>a</sup>The mobility is calculated from  $\sigma=1/(q\rho n)$ 

Additionally, by increasing the boron atomic density with higher boron sputtering power, the electrically active doping concentration increases from  $2.5 \times 10^{+18}$  cm<sup>-3</sup> to  $1.4 \times 10^{19}$  cm<sup>-3</sup>. However, this concentration tends to saturate in the range of  $1 \times 10^{19} - 2 \times 10^{19}$  cm<sup>-3</sup> when the boron sputtering power is between 10 W and 15 W. We note that the atomic concentration achieved by this high boron sputtering power should be over  $5 \times 10^{+20}$  cm<sup>-3</sup>, [19, 34]. This concentration has already reached the boron solubility limit in silicon of around  $2.5 \times 10^{20}$  cm<sup>-3</sup> after 1050 °C annealing, [140] the saturated electrically active doping density is at least one order of magnitude lower.

There are two possible reasons for the lower saturation of boron doping concentration:

(1) Smaller ncSi cannot be boron doped even at higher doping levels, which is similar to what is observed with phosphorous doping in small ncSi. [23] This can be further confirmed by the PL emission and the PL blue shift at very high doping, as discussed in section 4.3.

(2) At higher boron doping level, a large amount of excess boron atoms may stay in the dielectric matrix and aggregate at the ncSi interface, rather than working as active dopants. The excess boron may only induce more defects at the interfaces [28] deteriorating the PL emission [39] and the carrier transport in ncSi films.

It is also important to note that the doping concentrations estimated by CV measurements does not necessarily represent the free carrier concentration.[130]

By considering the high ionization energy in boron doped ncSi and the large amount of deep level defects and traps. [141] the free carrier concentration should be lower in the absence of the large external voltage bias. Therefore, the doping concentration evaluated by CV measurement only represents the electrically active doping in turn causing an under-estimation of the actual carrier mobility.

To properly fit the measured CV curves as shown in Figure 4.11, the density and distribution of interface traps ( $D_{it}$ ) has to be taken into account by Equation 4.10 - 4.12. We find that it is possible to fit the CV stretch only by using a U-shaped interface trap density distribution as described for a-Si. [142]



**Figure 4.12:** Interface traps distribution results.  $D_{ita}$  means the acceptor-like traps density and  $D_{itd}$  means the donor-like traps density.

According to the extracted distribution of  $D_{it}$  as shown in Figure 4.12, there are more deep level interface traps in the relatively low doped ncSi (B5W) than in the

highly doped ncSi (B10W and B15W). For highly doped ncSi, the  $D_{it}$  density near the band edge increases dramatically and the donor-type traps ( $D_{itd}$ ) near valence band edge ( $E_v$ ) dominate. The high  $D_{it}$  value not only confirms a poor SiO<sub>2</sub> and ncSi interface, but also indicates that the ncSi layer may contain a large amount of defects after high temperature annealing and forming gas passivation.

In terms of the carrier mobility, as long as the linear relationship between the doping concentration (n) and conductivity ( $\sigma$ ) is applicable,  $\sigma$ =q $\mu$ n, we are able to calculate the effective mobility using  $\mu$ = $\sigma/(qn)$ . From the high electrically active doping concentration and effective mobility results shown in Table 4.1, it is clear that the electrical conduction in B doped ncSi is limited by carrier transport. The calculated effective mobility is about 4 to 5 orders of magnitude lower than the mobility of crystalline Si at a similar doping level. [137] It should be noted that the factors determining the carrier transport in hybrid ncSi/SiO<sub>2</sub> low dimensional materials are totally different from those of crystalline silicon.

In the lower dimensional ncSi materials, there are many possible factors limiting the mobility, such as (1) low tunnelling probability through SiO<sub>2</sub> barrier, (2) carrier trapping during hopping through the defects in SiO<sub>2</sub> and ncSi/SiO<sub>2</sub> interface, and (3) strong scattering from the defects induced by the excess boron. [28] The strong scattering from excess dopants and defects can be confirmed from the effective mobility decreasing with higher boron density. It is also conceivable that the defects induced by the high excess boron density can further deteriorate the material lifetime so as to dramatically reduce the photovoltaic device  $V_{oc}$ . [116] In order to increase the carrier transport, ncSi in  $SiO_2$  with high interconnectivity and intimate contacts with each other can be used by increasing the Si content in the SRO layer. This effectively reduces  $SiO_2$  barrier width and forms conduction paths. However, the quantum confinement effect will be relaxed compared to the well isolated ncSi.

It is more important to increase the doping efficiency in ncSi in order to fundamentally reduce the dopant density generally used to achieve acceptable conductivity, so as to reduce the excess dopant density. The reduced excess dopant density not only can reduce the dopants aggregation at ncSi interface, but will also reduce the defects/traps formation and carrier scattering effects. Doping ncSi by thermal diffusion [143] could be a promising doping method because the reported effective mobility of  $2.2 \text{ cm}^2/\text{V/s}$  is almost three orders of magnitude higher than the mobility of the in-situ doping method described in this chapter.

#### 4.7. Conclusion

In this chapter, we have studied the CV characterization on boron doped ncSi materials by developing an inverted MOS structure device. The use of an inverted MOS structure device overcomes the parasitic effects, such as the large sheet resistance and the edge effects, so that it is possible to perform CV measurement on the highly resistive ncSi (SiO<sub>0.66</sub>) thin film materials (200-400  $\Omega$ ·cm).

Although some frequency dispersion is observed, this can be eliminated by considering a lossy dielectric layer between the ncSi and the gate oxide. By fitting

the high frequency CV results using the numerical model presented, we have evaluated the doping type, doping concentration, interface traps.

It is found that the in-situ boron doped ncSi showed high electrically active doping concentration ranging from  $2.5 \times 10^{18}$  to  $1.4 \times 10^{19}$  cm<sup>-3</sup> with increasing boron density. However, the doping efficiency is still below 5%. The relatively high Si content we used may bring about the formation of a Si network and narrow spacing between ncSi, which could be the reason for the relatively higher doping concentration and doping efficiency compared to the observations in phosphorus doped material.

Further increasing the boron density will not increase the electrically active boron doping but only introduces more defects resulting in PL quenching and lower effective mobility results. The saturation of doping at around  $1x10^{19} - 2x10^{19}$  cm<sup>-3</sup> has also been observed. The reasons for this observed saturation can be the extremely low possibility of doping of small ncSi and the aggregation of large amounts of inactive boron dopants at the dielectric matrix (SiO<sub>2</sub>) and ncSi interface.

The calculated effective carrier mobility has been found to be 4 to 5 orders of magnitude lower than that of crystalline Si. The low possibility of carrier tunnelling through  $SiO_2$  barrier, the stronger scattering effect from high excess impurity density and the deep level defects/traps at ncSi interface could be the main reasons to hinder the carrier transport in ncSi films. Therefore, it is of utmost

importance to improve the doping efficiency in order to reduce the excess dopant density and defects/traps in ncSi.

The CV characterization method presented in this chapter offers a reliable way to evaluate the electrical properties of doped ncSi. Further applying the CV method on doped ncSi and comparing the different doping methods will help to understand and improve the ncSi electrical properties for photovoltaic and photonic applications.

### **Chapter 5**

## Pulsed KrF Excimer Laser Dopant Activation in Nanocrystal Silicon in a Silicon Dioxide Matrix

**This chapter is based on the publication:** Zhang, T., Simonds, B., Nomoto, K., Puthen Veettil, B., Lin, Z., Perez Wurfl, I., and Conibeer, G.: 'Pulsed KrF excimer laser dopant activation in nanocrystal silicon in a silicon dioxide matrix', Appl. Phys. Lett., 2016, 108, (8), pp. 083103

**Overview:** In this chapter, we show that the free carrier concentration in ncSi can be improved by more than one order of magnitude using a single excimer laser pulse. The pulsed laser annealing (PLA) shows promising results, increasing the carrier concentration without the need to increase the dopant concentration. Hall Effect and temperature dependent Hall characterization are used to elucidate details on carrier transport and doping effects in ncSi. We propose that the improved electrical properties are a result of interstitial phosphorus/boron dopant activation, impurities that can be found inside the ncSi. Additionally, structural characterization using Raman spectroscopy and AFM also confirm no film ablation or ncSi melting. By improving doping efficiency, PLA is a potential process to reduce the detrimental effects of doping in ncSi as it provides a means to achieve a higher doping with less dopant atoms compared to other doping methods.

#### 5.1. Introduction

As discussed in previous chapters, although the doping in ncSi is possible, the low doping efficiency of ncSi in SiO<sub>2</sub> causes low conductivity and detrimental effects to the material quality. The incorporation of electrically active p- and n-type impurities is necessary in order to realize ncSi-based junction photovoltaic devices. [144, 145] Therefore, low doping efficiency is an issue that needs to be solved for further ncSi based solar cell development.

Low doping efficiency in ncSi has already been generally identified as one of the most important limiting factors hindering the development of practical ncSi devices, [23, 33, 116] but there is no effective method so far reported to possibly tackle this problem. In addition to the most generally used doping method of insitu dopant incorporation in SRO, intensive research efforts have also been made to investigate and develop other doping methods for improved the doping of ncSi, including ion implantation, [146] thermal diffusion, [143] modulation doping [96, 147] and using other doping atoms besides B and P. [148]. Although it is difficult to quantitatively compare the doping properties from different doping methods due to variations in ncSi structure, impurity configuration, and characterization techniques, the ineffectiveness of doping is clear based on the commonly observed low conductivities at high impurity atomic concentrations as well as the reduction of the photoluminescence due to doping effects. [20, 21, 126, 146]

A self-purification mechanism has become the most widely accepted explanation for the low doping efficiency in quantum confined silicon structures, [32, 117, 149] which comes about due to the extremely high dopant bond formation energy, coupled with an increase in the carrier activation energy for common silicon dopants (boron and phosphorus). As predicted by many theoretical calculations, [26, 28, 32, 141] this effect has been experimentally confirmed in recent years by atom probe tomography (APT). Gnaser et. al have clearly identified the aggregation of large amount of phosphorus dopants at the ncSi/matrix interface regions. [22] Coupled with electron paramagnetic resonance (EPR) information showing low electrically active doping concentration [23, 24], it can be inferred that these dopants at the interface are electrically inactive, which results in a low doping efficiency.

However, an important observation of APT results is the remarkable amount of dopants that exist inside the crystallite Si region of ncSi. [22, 32] Both B and P atoms are found inside ncSi in a notable quantity, although the majority of the dopants are found to reside in the dielectric matrix. These results can be clearly seen in Figure 5.1 from the test of a p-i-n ncSi based solar cell (TEM cross-section structure as shown in Figure 5.1 (a)) by APT measurement. This finding, together with the realization of the existing electrically inactive dopants inside ncSi, [32, 33] leads to the utilization of pulsed laser annealing for dopant activation.



**Figure 5.1:** (a) The cross section TEM of p-i-n ncSi solar cell. (b) The proxigram results of B/P doped ncSi interface. Each point is the average concentration value of 1 nm spatial depth. The results are from Keita Nomoto (UNSW) with permission for presentation.

In the microelectronic industry, pulsed laser annealing (PLA) has been regarded as an effective approach to re-activate the large amount of electrically inactive dopants introduced by ion-implantation and diffusion in very shallow, highly doped junctions. [150-152] In nanotechnology, PLA has also been used on freestanding Si nanowires for the activation of ion-implanted [153] and spun-on dopants [154]. In both of these works, dopant activation has been inferred from resistivity measurements, which shows an improvement in electrical conduction after PLA treatment.

Improved doping efficiency in ncSi would be marked by an increase in free-carrier concentration without excessive impurity concentration, leading to an increase of electrical conductivity. In this chapter, we report an increase of more than one order of magnitude in conductivity and free-carrier concentration due to PLA applied to a quantum confined Si system.

#### 5.2. Sample Preparation and Pulsed Laser Annealing

The boron and phosphorus doped ncSi samples are fabricated by a radio-frequency magnetron sputtering method whereby 40 alternating bilayers of 3.5 nm silicon rich oxide (SRO) and 1.5 nm stoichiometric SiO<sub>2</sub> are deposited on a quartz substrate. [19, 72] The doping impurities, either phosphorus (P) or boron (B), are co-sputtered into the SRO layer by using  $P_2O_5$  and Boron targets. The RF-power applied on  $P_2O_5$  and Boron targets are 4W and 5W respectively. Then, through high-temperature furnace annealing at 1150 °C for 1 hour in pure N<sub>2</sub> ambient, Si nanocrystals are formed as identified in Figure 5.2. From the TEM Plasmon image of Figure 5.2 (a), the ncSi size varies over a wide range (4 to 40 nm) and no multilayer structure can be identified. This can be attributed to the enhanced silicon agglomeration due to high temperature annealing and relatively high silicon content in the SRO.

In order to avoid the low conductivity due to carrier transport blockage by the large dielectric barrier spacing between ncSi, a relatively high silicon content in the SRO (SiO<sub>0.47</sub>) has been used to form a closely packed and interconnected ncSi network.



**Figure 5.2:** (a) The cross section TEM Plasmon image of the P doped ncSi after furnace annealing (no pulsed laser). The white regions are Si clusters in various sizes. (b) The HRTEM image directly showing the existence of interconnected silicon nanocrystals (the lattice fringes).



**Figure 5.3:** Atomic probe tomography results of the (a) 3D structural details of ncSi, (b) Identification of isolated ncSi, (c) identification of connected ncSi, and (d) the proxigram of the boron distribution across the ncSi interface.

The 3-dimensional structure of a B-doped sample before PLA (after thermal annealing) has been characterized by atom probe tomography (APT). From Figure 5.3 (a), it is clear that our ncSi is of the interconnected type. By further analysing the 3-D model, the isolated ncSi and interconnected ncSi can be both identified in Figure 5.3 (b-c). The shape of the isolated ncSi is not that of a sphere but rather a sponge like structure.

The APT proxigram in Figure 5.3 (d) shows the atomic concentration (at. %) of boron decreasing upon entering the crystalline region, but there is still a significant concentration within the crystallite as well as in the approximately 1 nm thick interface region (SiO<sub>x</sub>). The interface (X-axis=0) is defined by a silicon density of 28.44 atoms/nm<sup>3</sup> considering a detector efficiency of 0.57, which is equivalent to a bulk silicon density of 49.9 atom/nm<sup>3</sup>. This APT analysis is qualitatively similar to that on phosphorus doping previous reported by Gnaser, *et al*, with the main difference being that P atoms aggregates more at the interface than our results show for B [22]. With the ncSi regions defined, the boron atomic concentration in ncSi can be estimated by dividing the integral of the boron atoms within all the ncSi by the total volume of ncSi. From the APT data measured, the boron concentration in ncSi is approximately  $3x10^{+20}$  cm<sup>-3</sup> or more.



**Figure 5.4:** (a) the laser beam uniformity tested by CCD sensor array. (b) The schematic pulsed laser annealing system.

The pulsed laser treatments on the doped ncSi thin film was performed in ambient air conditions with an excimer KrF laser (248 nm) with 22 ns pulse duration (full width at half maximum). Single and multiple laser pulses have been used for each annealing process. The pulsed laser is configured at 1 Hz repetition rate. At this low frequency, the annealing process using multiple pulses is easily done by replacing the power sink with the sample, counting the number of pulses and then removing the sample out of the laser beam when the desired number of pulses has been reached. A fly's eye homogenizer has been used to create a flattop beam that was 2.9 x 2.9 mm<sup>2</sup> when focused on the sample with a single planoconvex lens of focal length 100 mm. The beam dimension is defined at 50% of the peak value at the beam edge and the intensity of the flattop portion of the beam varies by less than 10%. Four standard levels of laser fluence (mJ/cm<sup>2</sup>) have been defined and measured. These are  $202 \pm 5$  mJ/cm<sup>2</sup>,  $156 \pm 4$  mJ/cm<sup>2</sup>,  $101 \pm 2$  mJ/cm<sup>2</sup> and  $70 \pm 3$  mJ/cm<sup>2</sup>. For this experiment, four samples have been annealed at these specific laser fluence, plus one without laser treatment labelled as 0 mJ/cm<sup>2</sup> (only furnace annealed).

#### 5.3. Structural Characterization after Pulsed Laser Annealing

For pulsed laser thin film material processing, it is important to prevent film ablation due to the transient strong local radiation. [51] Atom force microscopy (AFM) has been used to investigate the surface roughens to assess whether film ablation happened. As shown in Figure 5.5 and 5.6, the surface morphology after a high laser fluence of  $202\pm 5$  mJ/cm<sup>2</sup>, the average surface roughness of B/P doped ncSi are only 1.29nm and 0.9nm, respectively. For comparison, the ncSi sample only annealed by furnace show average surface roughness as 2.36 nm as presented in Figure 5.7. The low surface roughness from AFM measurement confirms neither ablation nor surface melting occurred. This result is important to demonstrate the feasibility of PLA as a potential annealing tool to modify ncSi electrical and optical properties without causing an undesirable surface morphology change.



**Figure 5.5:** The AFM results of boron doped ncSi after  $202\pm 5 \text{ mJ/cm}^2$  annealing. The average roughness is about 1.29nm



**Figure 5.6:** The AFM results of phosphorus doped ncSi after  $202\pm 5$  mJ/cm<sup>2</sup> annealing. The average roughness is about 0.9nm.



**Figure 5.7:** The AFM results of phosphorus doped ncSi after only furnace annealing. The average roughness is about 2.36nm.

The crystallinity of ncSi before and after PLA has been investigated by micro-Raman spectroscopy. The Raman spectra in Figure 5.8 shows the typical features of ncSi, consisting of a main peak ( $509 - 510 \text{ cm}^{-1}$ ) and a slight increase in the disorder band ( $350 \text{ cm}^{-1} - 500 \text{ cm}^{-1}$ ) from a PLA-induced amorphous phase. After PLA treatment, a slight increase of the disorder band is noticeable being more obvious for higher laser influence.

By fitting the Raman spectra with one asymmetrically broadened lineshape for the phonon-confined TO-LO mode from cSi near 520 cm<sup>-1</sup> and two Gaussian-like disordered bands from amorphous/disorder contributions, [68] the degree of crystallinity shown in the inset can be calculated by

$$f_C = \frac{I_C}{I_C + \gamma I_a} \tag{5.1}$$

where  $I_c$  and  $I_a$  are the integrated intensities of the crystalline and amorphous silicon (aSi) phases, respectively. The relative Raman cross-section ( $\gamma$ ) of the cSi phase with respect to the aSi phase is 0.1 due to the high Si content used. [69]

From the quantified crystallinity results shown in the inserted charts in Figure 5.8 (a) and (b), the phosphorus doped ncSi  $f_c$  only decrease from 85% to 79% with increased laser power density. The boron doped ncSi shows merely a 5% decrease from 89% to 84%. By considering the relative Raman cross-section ( $\gamma$ ) of cSi with respect to the aSi phase to be 0.1, a relatively small generation of aSi by PLA ought to cause a much stronger increase of the disorder band (350 cm<sup>-1</sup> – 500 cm<sup>-1</sup>), resulting in a notable drop in crystallinity. This is not observed in our samples as shown in Figure 5.8, and it indicates that at the laser fluences used, the ncSi material is still very much crystalline albeit with a smaller increase in disorder, presumably at the ncSi interface region. Since this change is gradual, it also suggests that the material is unlikely to melt or undergo rapid recrystallization by PLA, which would causes an abrupt change in crystallinity at some threshold fluence.



**Figure 5.8:** Experimental Raman spectra of phosphorus (a) and boron (b) doped ncSi. The calculated crystallinity results (inset) are obtained by fitting the Raman spectra using the asymmetric lineshape of phonon-confined TO-LO mode for crystalline silicon (dashed line) and Gaussian functions accounting for the amorphous contributions (dotted lines). [155]

However, our result cannot exclude the possibility that using higher laser fluence will turn silicon crystals to amorphous silicon. The appearance of amorphous silicon would considerably change the electrical properties of ncSi. In such a case, a reduced electrical conductivity is expected due to stronger scattering effects and reduced carrier concentration by deep level traps/dangling bonds/defects [156]. In order to improve the doping effects in ncSi, the formation of amorphous silicon by pulsed laser should be avoided.

#### 5.4. Identification of Dopant Activation by PLA

The direct identification of improved doping is shown in Figure 5.9 as an increased conductivity and free carrier concentration values for both B and P doped ncSi after PLA, which has been obtained from Hall Effect measurements using the Van der Pauw technique. With the application of just a single 22 ns laser pulse, the electrically-active P/B dopant concentration has been improved by more than one order of magnitude. To be more specific, the increase is largest for phosphorous doped ncSi after 202 mJ/cm<sup>2</sup>, which becomes 25 times higher than furnace annealing alone.

Although the doping concentration reaches a degenerate level ( $\sim 10^{20}$  cm<sup>-3</sup>), the conductivity is still limited by a low effective mobility (Figure 5.9 (b)) which varies between 0.1 and 0.6 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. The slight reduction of effective mobility with laser fluence is consistent with increased scattering from an increase in electrically active dopants. We should point out that, the increase in disordered as shown in the Raman results can also contribute to the lower mobility. Although the carrier concentration and the effective mobility show opposite trends with laser

fluence, there is no doubt that the conductivity (Figure 5.9 (c)) is a strong function of the laser fluence. As no extra impurities are added, the increased carrier concentration and conductivity indicates a higher doping efficiency.

Multiple pulse irradiation (1, 3 and 5) has also been applied for dopants activation. Preliminary results of this process are shown in Table 5.1 and Table 5.2. The reduction in resistivity and the increase in doping concentration can be more obviously discerned for the 155mJ/cm<sup>2</sup> case rather than the 70 mJ/cm<sup>2</sup> and 101 mJ/cm<sup>2</sup> cases. However, it is clear that the improvement in electrical properties strongly depends on the laser fluence rather than the pulse numbers. One possible reason is that the highest temperature achievable is proportional to the laser fluence and the peak temperature determines the degree of dopant activation. As the temperature measurement in the nanosecond timescale in practice is very difficult, establishing a material heat transfer/thermal model to extract thermal process will help to further understand the pulsed laser annealing mechanisms [157, 158].



Figure 5.9: The pulsed laser annealing effects on (a) free-carrier concentration, (b) mobility and (c) conductivity (Lines are guided for eyes). [155] The error bar is based on 20 repeated measurements.

Table 5.1: Boron doped n	cSi
--------------------------	-----

Laser fluence	Pulse number	Resistivity (Ω·cm)	Doping concentration (#/cm <sup>3</sup> )
	1	0.54	$7.30 x 10^{+19}$
156 mJ/cm2	3	0.41	$8.00 \text{ x} 10^{+19}$
	5	0.38	$9.00 \text{ x} 10^{+19}$
	1	0.83	4.50 x10 <sup>+19</sup>
70 mJ/cm2	3	0.71	$5.00 \text{ x} 10^{+19}$
	5	0.70	$6.20 \text{ x} 10^{+19}$

\* NOTE: The results are averaged values.

Table 5.2: Phosphorus doped ncSi.						
Laser fluence	Pulse number	Resistivity (Ω·cm)	Doping concentration (#/cm <sup>3</sup> )			
	1	8.10 x10 <sup>-2</sup>	$3.0 \text{ x} 10^{20}$			
156 mJ/cm <sup>2</sup>	3	7.13 x10 <sup>-2</sup>	$2.7 \text{ x} 10^{20}$			
	5	7.03 x10 <sup>-2</sup>	$2.7 \text{ x} 10^{20}$			
	1	2.40 x10 <sup>-1</sup>	8.8 x10 <sup>19</sup>			
101 mJ/cm <sup>2</sup>	3	2.08 x10 <sup>-1</sup>	9.2 x10 <sup>19</sup>			
	5	1.99 x10 <sup>-1</sup>	$1.1 \text{ x} 10^{20}$			
	1	3.70 x10 <sup>-1</sup>	4.3 x10 <sup>19</sup>			
70 mJ/cm <sup>2</sup>	3	4.22 x10 <sup>-1</sup>	2.2 x10 <sup>19</sup>			
	5	3.75 x10 <sup>-1</sup>	3.0 x10 <sup>19</sup>			

\* NOTE: The results are averaged values.

#### 5.5. Discussion on ncSi Doping and Carrier Conduction

A very unique feature of the pulsed laser annealing on doped ncSi is that the electrically activated doping concentration is increased without varying the atomic dopant concentration or ncSi structure. Therefore, the changes in electrical properties should be only related to the reconfiguration of dopants in the ncSi material.

As shown in Figure 5.10 (a), the doping concentration (n-type) for each laser fluence is largely temperature-independent from 150 K to 350 K, which confirms degenerate doping [144] as also indicated by APT and CV results (Chapter 3). Specifically, the doped ncSi by PLA at 202 mJ/cm<sup>2</sup> and 156 mJ/cm<sup>2</sup> shows a metallic behaviour. However, at lower laser fluence, the conductivity ( $\sigma$ ) weakly increases with temperature (Figure 5.10 (b)). This weaker temperature dependence is best fit by a log ( $\sigma$ ) ~ T<sup>-1/4</sup> behaviour indicating hopping transport via localized states. This has been identified as the predominant conduction mechanism in disordered semiconductors. [159-161]



**Figure 5.10:** (a) Temperature-dependent Hall measurement results of phosphorus doping concentration over the temperature range from 150 K to 350 K. The flat solid line is an aid to show that there is little to no temperature dependence in doping concentration. (b) A T-1/4 fitting plot of conductivity of phosphorus-doped ncSi annealed by different laser fluences from 0 mJ/cm2 to 202 mJ/cm2. [155]

Hopping transport can be described in a simplified thermally activated hopping law originally proposed by Mott:

$$\sigma(T) = \sigma_0 exp\left[\left(\frac{T_0}{T}\right)^{-p}\right]$$
(5.2)

where  $\sigma_o$ ,  $T_o$ , and p are constants depending on temperature, degree of disorder, details of Coulomb interactions, and the dimensionality of system. [160] Following Mott's approach, [162, 163]  $\sigma_o$  is a power function of the density of states at Fermi level ( $N(E_F)$ ) and temperature (T), and  $T_o$  is inversely proportional to  $N(E_F)$  as a measure of the degree of disorder in the film:

$$\sigma_o \sim N(E_F)^{3/4} T^{-1/4} \tag{5.3}$$

$$T_o \sim \left[\frac{a^3}{k_B N(E_F)}\right] \tag{5.4}$$

where  $k_B$  is the Boltzmann constant and  $\alpha$  is the decay rate of the wavefunction. This means an increase in  $N(E_F)$  will directly increase the conductivity, and reduce the temperature dependence as  $T_o$  decreases. Therefore, the results of the higher doping concentration and the disappearance of the temperature dependence in the conductivity with increasing laser fluence can be explained by the increased  $N(E_F)$ as the Fermi level approaches the mobility edge. [164] Here we proposes that more electrically active donor states have been generated by PLA. Therefore, it is likely that a donor impurity band [164] is formed, especially after PLA at 202 mJ/cm<sup>2</sup> and 156 mJ/cm<sup>2</sup>, which explains metallic conduction behaviour. However, the hopping transport, even though it shows metallic behaviour, is fundamentally determined by degree of disorder, Coulomb interactions and hopping distance and energy, which has much lower carrier mobility. This is consistent with most experimental results of doped ncSi.



**Figure 5.11:** Photoluminescence (PL) results of highly phosphorus (a) and boron (b) doped ncSi by PLA process, which show red-shift by higher laser fluence. (c) The PL intensity as a function of laser power density. [155]

In addition to the electrical characterizations, photoluminescence (PL) measurements were also undertaken and are shown in Figure 5.11. The B and P doped ncSi show a PL red-shift as PLA laser fluence increases. As there should be

no nanocrystal size change or dopant impurity redistribution in ncSi after PLA, the PL red-shift can be attributed to the reduction of the effective bandgap as band tails extend towards mid-gap or to impurity band formation when more localized states exist near the mobility edge. This corroborates the activation of interstitial dopants to substitutional dopants as more localized donor/acceptor states are generated. In Figure 5.11 (c), the integrated PL intensity decreases with laser power density, which can be due to the Auger recombination from the higher doping concentration achieved. However, it is also possible that more defects are generated by PLA. Therefore, the investigation of passivation after PLA, like forming gas annealing (H<sub>2</sub>), is still critical for the material quality.

#### 5.6. Mechanisms of Dopant Activation by PLA

To explain the increase in electrically active doping in ncSi by PLA, two other possible mechanisms are included:

1) The very high temperatures created by PLA causes dopants to diffuse into the ncSi region where they are simultaneously activated.

2) The PLA acts to activate interstitial dopants already within the ncSi crystallite region.

Although we have not experimentally determined if diffusion or dopant redistribution happens while pulsed laser annealing, the diffusion lengths of the dopants in ncSi embedded in SiO2 should be extremely short, which will not be effective to improve doping. We will then assume that diffusion only happens in the solid state as no sign of the material melting has been observed. By using 1600 °C as the melting point of pure SiO<sub>2</sub> as an upper temperature bound, and using literature values for diffusivity and activation energy of P [165] and B [166] in SiO<sub>2</sub>, we can calculate a diffusion length of  $2 \times 10^{-3}$  nm for P and  $3 \times 10^{-4}$  nm for B during 10 ns annealing process. Therefore, it appears very unlikely that, in the absence of melting, dopants within the SiO<sub>2</sub> matrix or even interface will diffuse into the nanocrystals during PLA.

Therefore, it is more likely that the activated dopants originate from interstitial sites within the crystallite region. For most of the doped ncSi after furnace annealing, the a) existence of dopant inside ncSi, as shown in APT measurements in Figure 5.1 and 5.3 as well those of others, [22] and b) EPR results showing that the majority of them are electrically inactive, [24] together indicate a substantial number of these dopants should be at the interstitial sites. This has furthermore been confirmed by density functional theory calculations [32] and implied from the transient current measurement of P doped ncSi. [33]

This interstitial dopant model explanation does not actually contradict the selfpurification mechanism. [117, 149] It is because self-purification models only considers a substitutional configuration and not interstitial. [31, 117] As bond breaking is not required for interstitial dopants, the formation energy should be less than substitutional dopants. [32] Therefore, the high temperature and strong heat fluence created by PLA can possibly promote such transitions. Then, owing to the fast cooling rates ( $\sim 10^{+10}$  K/s) inherent to the PLA process, the activated dopants are trapped and do not revert to interstitial sites. Another possibility for dopant activation is that the 5 eV high photon energy of the excimer laser are able to cause solid phase chemical reaction for transferring interstitial dopants to substitutional sites. [28] This could be simply verified by using a pulsed green laser, some of the future work to come after this thesis.

#### 5.7. Conclusion

We have demonstrated that a pulsed excimer laser treatment is a viable postfurnace-annealing process to improve doping efficiency of B and P doped ncSi in SiO<sub>2</sub>. This has been experimentally evidenced by the improved conductivity and electrically activated dopant concentrations for boron and phosphorus. Specifically, at 202 mJ/cm<sup>2</sup>, the activated dopant concentrations for boron and phosphorous show more than one order of magnitude increase. Additionally, at this laser energy density and below, there is no significant film ablation or ncSi structure change by melting. The increased doping concentration produced by PLA dominates the measured improved conductivity. Although a degenerate doping level (~10<sup>+20</sup> cm<sup>-</sup> <sup>3</sup>) is achievable by PLA, the relatively low conductivity is limited by the low effective mobility, which is consistent with the capacitance-voltage measurement of B doped ncSi results reported in **Chapter 3**. Temperature-dependent conductivity measurements suggest a hopping transport mechanism in our narrowspaced and interconnected ncSi. The metallic behaviour shown at higher laser fluence can be attributed to a donor impurity band formed from the increase in electrically active dopants. We argue that the activated dopants initially reside within the ncSi crystallite as interstitial impurities, which are excited to substitutional dopants during pulsed high temperature or by the high energy photons. In addition to ncSi, pulsed laser annealing has also potentially provided an alternative way to modify the impurity atomic configuration in other low dimensional semiconductor materials.

### **Chapter 6**

# Further Discussions, Conclusions and Future Work

**Overview:** In this final chapter, the electrical properties of doped ncSi material are further discussed, including carrier lifetime and carrier mobility, which also significantly limit the ncSi based photovoltaic device performance. The conclusion part summarizes each chapter's results. Finally, three interesting ncSi related research directions are presented: colloidal ncSi, pulsed laser process and ncSi based LED.

#### 6.1. Further Discussions

Compared to silicon nanocrystals in  $SiN_x$  and SiC, silicon nanocrystals embedded in  $SiO_2$  matrix have shown good size, shape and density control and very strong quantum confinement related photoluminescence, but very poor electrical conductivity. [167] The ability to dope ncSi embedded in  $SiO_2$  is an important challenge to overcome if this material is to be used in efficient photovoltaic devices. The most significant issues regarding the doping of ncSi have been addressed in the previous chapters of this thesis, namely an effective way to characterise doping using capacitance-voltage measurements (Chapter 4) and a method to improve the activation of dopants in ncSi using a pulsed KrF excimer laser (Chapter 5). The motivation for the research presented in this thesis has come about from the realization that ineffective doping and low carrier mobility are the most important factors limiting the photovoltaic performance of ncSi. (Chapter 3). Further discussions on the electrical properties of doped (B/P) ncSi for photovoltaic performance are presented in this section.

#### **6.1.1. Importance of carrier lifetime**

The inferior photovoltaic performances of most ncSi based solar cells to date, based on the low  $V_{oc}$  and extremely low  $I_{sc}$  achieved thus far, have been generally attributed to the very high series resistance ( $R_s$ ) arising from the low conductivity of ncSi. [19, 168] in particular because of the lateral current flow present in these devices.

However, it should be noted that the large series resistance is only one of the limiting factors. Low minority carrier lifetime can be even more detrimental, resulting in an extremely low photogenerated current ( $I_{ph}$ ). An example of this is illustrated by the low  $V_{oc}$  and negligible  $I_{sc}$  achieved on a substrate-free ncSi based photovoltaic device fabricated as a floating membrane (ncSi active layer < 500 nm)
with electrodes on both sides as reported by Philipp et al. [169] This ultra-thin device utilised a vertical structure to avoid the large series resistance that results from lateral current flow. In this case, due to the low series resistance, it is safe to say to that measured short circuit current must be comparable to the photogenerated current ( $I_{sc} \approx I_{ph}$ ). Such a structure confirms that  $I_{SC}$  is indeed limited by the material quality rather than the device architecture. The high defect density in ncSi material is the main reason for low  $V_{oc}$  and  $I_{sc}$ . Additionally, the low lifetime in doped ncSi is due to the high deep defects/traps density. A clear indication of the deep defects in these materials is evidenced by the lower electronic bandgap extracted from PL and optical absorption measurements. [116] To the best of our knowledge, no photovoltaic devices made with ncSi have successfully demonstrated an efficient conversion of photon to current. This is consistent with the results reported in Chapter 3.

One important reason for the poor lifetime of doped ncSi is the low doping efficiency, which causes a large amount of excess impurities that aggregate in the SiO<sub>2</sub> matrix and at the ncSi surface. These excess impurities are believed to be electrically inactive, working as deep level defects/carrier traps. The low doping efficiency in ncSi has also been discussed in Chapter 4 and 5. To address the issue of low doping efficiency, we have studied a method to improve conductivity and carrier concentration of both B and P doped ncSi using a KrF pulsed laser as discussed in Chapter 5. We propose that with this approach, a lower doping density

can be used. This in turn potently improves the lifetime and could reduce dopant diffusion to the intrinsic active layer in a p-i-n structure during the usual high temperature annealing process.

## 6.1.2. Importance of carrier mobility

In bulk silicon solar cells, minority carrier mobility is rarely considered because it is high enough not to be the factor that limits photogenerated current. In contrast, the carrier lifetime can vary by orders of magnitude becoming then dominant limiting factor. However, for thin film solar cells, where the active material/layer may have a much lower minority carrier lifetime, the carrier mobility becomes an important factor if photogenerated carrier collection is to be improved.

In the case of ncSi, its low conductivity can be attributed to the lack of free carriers or/and low carrier mobility. The lack of free carriers can be due to a self-purification effect, high dopant ionization energy, and deep level traps. Improving the conductivity in ncSi is not necessarily achieved by using higher doping concentration in the SRO layer to obtain more free carriers (which may be further detrimental to minority carrier mobility). In the case of this material, the silicon content is an important parameter as well that may limit the conductivity even more than the doping. For example, in Chapter 4, a high electrically active doping concentration ( $\sim 10^{+19}$  cm<sup>-3</sup>) has been found in degenerate boron doped ncSi in SiO<sub>2</sub> as determined by CV measurements. In Chapter 5, an enhanced dopant activation

by pulsed laser annealing has been also achieved, reaching a carrier concentration of up to  $\sim 10^{+20}$  cm<sup>-3</sup>. However, the conductivity of these two cases is very different. The degenerately boron doped ncSi in Chapter 4 is severely limited by carrier mobility, which is more than two order of magnitude lower than that of the laser annealed sample. This low mobility is mainly attributed to lower Si content used in SRO causing larger ncSi spacing, so that low carrier transport is dominated by tunnelling and activated hopping (Chapter 1.4). If the minority carrier mobility is to be improved, both, the doping and the silicon content must be optimised.

Given the fact that low carrier mobility is inherent to ncSi embedded in SiO<sub>2</sub>, there are several aspects that maybe worth considering in the device design of ncSi solar cells:

- Using thin active layers (intrinsic ncSi layer) for collecting minority carriers before they recombine (with the assumption that ncSi can be made strongly absorbing due to it pseudo-direct bandgap).
- Using p<sup>+</sup>-i-n<sup>+</sup> diode structure with controlled dopant diffusion to avoid degradation of intrinsic layer.
- Defects passivation with forming gas (Ar : H<sub>2</sub>) or gentle hydrogen plasma treatment.

Furthermore, the mobility itself can be improved by lowering the doping density but improving conductivity by using pulsed laser annealing, to reduce impurity scattering and defects formation.

#### 6.1.3. Summary of factors limiting PV performance

This section has further discussed the importance of carrier lifetime and carrier mobility as the limiting factors in the photovoltaic performance of ncSi based device. In addition to reducing series resistance, the improvement of carrier lifetime and mobility must be considered as well in order to improve the photogenerated current and V<sub>oc</sub>. Lower doping density, higher doping efficiency, relatively higher Si content and hydrogen defects passivation are recommended for further improving of ncSi solar cell fabrication.

## 6.2. Conclusions

This thesis focuses on the experimental investigations of silicon nanocrystals embedded in SiO<sub>2</sub> for photovoltaic applications. For the realization of all-Si tandem solar cells, a detailed study of ncSi synthesis by PECVD and photovoltaic device fabrication and characterizations have been presented. Although the basic principles of quantum confined silicon nanocrystal solar cells are simple (Chapter 1 and Chapter 2), the actual device design, the doping of ncSi and the electronic transport properties show complex technological and theoretical challenges. The main reasons are the insulating nature of the SiO<sub>2</sub>, the low doping efficiency and the complex structural and local atomic arrangement of silicon nanocrystals. By knowing the importance of electrical properties of ncSi, particular research emphasises has been placed on the development of Capacitance-Voltage characterization of doped ncSi and on pulsed laser annealing for dopant activations.

In Chapter 3, plasmas enhanced chemical vapour deposition (PECVD) has been demonstrated as a feasible technique for silicon nanocrystal fabrication. Detailed PECVD process parameters have been summarized and discussed for controlling the SRO stoichiometry and achieving a low deposition rate, which are essential to achieve superlattice ncSi structure. The most significant material feature of SRO fabricated by PECVD is the large amounts of nitrogen and hydrogen related compounds identified by XPS and FTIR, which is different to that of SRO fabricated by RF-sputtering. The nitrogen (N) incorporation in SRO not only hinders the ncSi crystal formation process during thermal annealing, but it also influences the electrical properties of ncSi. Although it is generally believed that the hydrogen (H) in SRO benefits the material quality by defects passivation, the ncSi materials after high temperature thermal annealing exhibit more defects, which can be due to the strong hydrogen effusion. This effect has been identified based on the increased refractive index and optical absorption of PECDV films. In addition to the material characterization, a rapid thermal annealing limited to 40 seconds has been investigated to show that the silicon crystallization in SRO is a fast process once high peak temperature over 1100 °C can be reached.

The boron and phosphorus doping in ncSi can dramatically reduce the resistivity by in-situ doping and diffusion doping methods. For in-situ doping in ncSi, the phosphorous doped ncSi shows much lower resistivity than boron doped ncSi. By analysing the effects of silicon content and doping concentration on the resistivity, it is evident that phosphorous can enhance the silicon crystallization but not boron. The doping of ncSi by diffusion using B and P was also investigated purely based on studying resistivity.

After demonstrating the ability to produce doped ncSi by PECVD, single junction ncSi photovoltaic devices have been fabricated and analysed as this represented an important step to the all-Si tandem solar cell. The detailed fabrication process and device characterization results are presented. The working devices exhibit diode I-V characteristics. An open circuit voltage of 230mV has been achieved. However, the devices exhibit extremely low short circuit current severely limiting the performance of these devices as efficient solar cells. The parameters extracted from electrical measurements indicate the photovoltaic performance is limited by the low current transport resulting from the high sheet resistance and the strong non-radiative recombination arising from the high doping concentration. These limiting factors can be attributed to the ineffective doping (low doping efficiency) in ncSi, which is a general problem for semiconductor nano-materials. Although the ncSi fabricated by PECVD is expected to have improved quality due to the expected lower defect density. The results however, indicate the problematic properties detrimentally challenging the photovoltaic application are similar to those found in ncSi fabricated by the more common RF-sputtering method.

By identifying the lack of reliable electrical characterization methods applicable to ncSi for the evaluation of electrically active dopants, a CV characterization method has been established by developing an inverted MOS structure device as discussed in Chapter 4. It has been demonstrated that the inverted MOS structured device is able to overcome the parasitic effects, such as the large sheet resistance and the edge effects, so that it becomes possible to perform CV measurement on the highly resistive ncSi (SiO<sub>0.66</sub>) thin film materials (200-400  $\Omega$ ·cm).

In the discussion of the results of CV measurements, the observed frequency dispersion effects are discussed. These effects are attributed to the lossy dielectric layer between ncSi and the gate oxide or the extremely low majority carrier mobility. By fitting the high frequency CV results using the numerical model discussed, we have evaluated the doping type, doping concentration, interface traps and other characteristic electrical properties of the highly boron doped ncSi. Very high electrically active doping concentration ranging from  $2.5 \times 10^{+18}$  to  $1.4 \times 10^{+19}$  cm<sup>-3</sup> with increasing boron density have been observed. However, the doping efficiency is still below 5%. The relatively high Si content used may induce the formation of Si network and narrow spacing between ncSi, which could be the reason for the relatively higher doping concentration and doping efficiency compared with the phosphorus doping. However, further increasing the boron density does not increase the electrically active boron doping but only introduces more defects resulted in PL quenching and lower effective mobility results. This doping saturation at around  $1 \times 10^{+19}$  -  $2 \times 10^{+19}$  cm<sup>-3</sup> can be attributed to a) the extremely low possibility of doping in small ncSi and b) the aggregation of large amount of inactive boron dopants at the dielectric matrix (SiO<sub>2</sub>) and ncSi interface.

The calculated effective carrier mobility is 4 to 5 orders of magnitude lower than that of crystalline Si. Besides the low possibility of carrier tunnelling through SiO<sub>2</sub> barrier, the stronger scattering effect from high excess impurity density and the deep level defects/traps at ncSi interface have been proposed to be responsible for hindering the carrier transport in ncSi films. Having identified this problem we then focus our attention on improving the doping efficiency in order to reduce the excess dopant density and defects/traps in ncSi.

Chapter 5 shows the effectiveness of pulsed KrF excimer laser for dopant activation in nanocrystal silicon embedded in SiO<sub>2</sub>. A pulsed excimer laser treatment has been demonstrated as a viable post-furnace-annealing process that improves the conductivity and increases the electrically activated dopant concentration in both boron and phosphorus doped ncSi. The improvement increases with higher pulsed laser power. Specifically, at 202 mJ/cm<sup>2</sup>, the activated dopant concentrations for boron and phosphorous show more than one order of magnitude increase. We argue that the activated dopants initially reside within the ncSi crystallite as interstitial impurities, and are excited to substitutional dopants by the high energy photons. With careful structural characterization by AFM and Raman spectroscopy, it is further confirmed that there is no film ablation or ncSi structure change (amorphorization) due to melting of the silicon nanocrystals. Therefore, pulsed laser annealing potentially provides a new and effective way to modify the impurity atomic configuration in ncSi even other low dimensional semiconductor materials.

Furthermore, by using the pulsed laser annealing technique, the electrically activated doping concentration can be changed without varying the atomic dopant concentration or ncSi structure, so it helps to study the carrier transport mechanisms in doped ncSi. The temperature-dependent conductivity measurements suggest a hopping transport mechanism in our narrow-spaced and interconnected ncSi. The metallic behaviour shown at higher laser fluence can be attributed to a donor impurity band formed from the increase in electrically active dopants. However, in intrinsic ncSi or low doped ncSi generally, the conduction shows space charge limited behaviour, and is attributed to defect assisted tunnelling. As the carrier transport mechanisms in ncSi depends on the complex ncSi structure, dopant impurity involvements and external excitation, simply applying band conduction model and Arrhenius analysis cannot correctly explain the conduction behaviour of ncSi.

Finally, in the view of the results of this thesis, the importance of carrier lifetime and carrier mobility, and suggestions of device deign have been further discussed in term of the photovoltaic performance of ncSi based device. To further improve ncSi solar cell fabrication, reducing doping density by promoting higher doping efficiency, using relatively higher Si content and hydrogen defects passivation are recommended.

#### 6.3. Future Work

In this section we will present other areas where the knowledge acquired in this thesis could be applied to improve the performance of ncSi based devices.

#### 1) Colloidal silicon nanocrystal.

The silicon nanocrystal fabrication by high temperature solid state crystallization in silicon rich oxide show strong ncSi structural disorder, poor morphology control and requires a very high thermal budget. However, colloidal silicon nanocrystals fabricated by wet chemical synthesis methods have exhibited remarkable size selection, silicon nanocrystal morphology uniformity, low density of surface defects and extremely low thermal budget. [3] Colloidal quantum dots can be easily applied in a sensitized solar cell structure by replacing dye with quantum dots, which have attracted tremendous attention for the potential as a low-cost solar cells. [170, 171] Using layer-by-layer assembly methods, solid thin films of ncSi can be fabricated using functionalised colloidal silicon nanocrystals that will selfassemble with a spacing precisely controlled by the ligand length. [172] Although the doping in colloidal silicon nanocrystals is still a challenge, similar to ncSi formed by solid state crystallization, several doping methods such as modifying ligands and chemical modulation doping by solvent materials have shown the possibility of the electrical properties tuning. [173, 174] The development and understanding of colloidal based films could be further improved by applying the CV measurement technique and laser treatment discussed in this thesis.

# 2) Further investigation on the pulsed laser annealing on doped nanocrystals.

As discussed in the Chapter 1 and Chapter 5, pulsed laser annealing is markedly different from thermal annealing, rapid thermal annealing or flash lamp annealing. Considering the rapid rise of the use of lasers in industrial applications, it seems relevant to investigate the mechanisms of dopant activation by pulsed laser annealing. Advanced characterization techniques like APT [22] and ESR [23] as presented in this thesis, will help to achieve a detailed understanding of the local dopant redistribution and the electrically active states that could be achieved by pulsed laser annealing. In light of the preliminary diffusion doped ncSi results shown in Chapter 4, it is interesting to investigate if pulsed laser annealing works well with diffusion method because diffusion doping method will not change the ncSi morphology due to dopants during annealing (Figure 5.1).

The doping of nanostructured semiconductor materials is a general challenge, hindering the fabrication of electronic and optoelectronic devices. Therefore, in additional to silicon nanocrystal, we believe it would be worthwhile to apply this technique to both III/V nanocrystals as well as colloidal nanocrystals.

## 3) The silicon nanocrystal based light emitting diode.

The colour tuneable silicon nanocrystal based light emitting diode opens another research direction for the application of silicon nanocrystals. The direct bang gap characteristics of quantum confined ncSi makes the ncSi based LED feasible.

Several preliminary ncSi based LED demonstrations have been reported. [175-177] However, the optimisation of the material electrical properties and the device design require further development.

# REFERENCES

- [1] Canham, L.T.: 'Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers', Appl. Phys. Lett., 1990, 57, (10), pp. 1046-1048
- [2] Cullis, A., and Canham, L.: 'Visible light emission due to quantum size effects in highly porous crystalline silicon', Nature, 1991, 353, pp. 335-338
- [3] Cheng, X., Lowe, S.B., Reece, P.J., and Gooding, J.J.: 'Colloidal silicon quantum dots: from preparation to the modification of self-assembled monolayers (SAMs) for bio-applications', Chemical Society Reviews, 2014, 43, (8), pp. 2680-2700
- [4] Ekimov, A.I., Efros, A.L., and Onushchenko, A.A.: 'Quantum size effect in semiconductor microcrystals', Solid State Commun., 1985, 56, (11), pp. 921-924
- [5] Vatankhah, C., and Ebadi, A.: 'Quantum size effects on effective mass and band gap of semiconductor quantum dots', Res J Recent Sci, 2013, 2, (1), pp. 21-24
- [6] Conibeer, G., Green, M., Cho, E.-C., König, D., Cho, Y.-H., Fangsuwannarak, T., Scardera, G., Pink, E., Huang, Y., Puzzer, T., Huang, S., Song, D., Flynn, C., Park, S., Hao, X., and Mansfield, D.: 'Silicon quantum dot nanostructures for tandem photovoltaic cells', Thin Solid Films, 2008, 516, (20), pp. 6748-6756
- [7] Kuno, M.: 'Density of states': 'Introductory Nanoscience: physical and chemical concepts' (Garland Science, 2012)
- [8] Brus, L.: 'Electronic wave functions in semiconductor clusters: experiment and theory', The Journal of Physical Chemistry, 1986, 90, (12), pp. 2555-2560

- [9] Chukwuocha, E.O., Onyeaju, M.C., and Harry, T.S.: 'Theoretical studies on the effect of confinement on quantum dots using the brus equation', 2012
- [10] Ledoux, G., Guillois, O., Porterat, D., Reynaud, C., Huisken, F., Kohn, B., and Paillard, V.: 'Photoluminescence properties of silicon nanocrystals as a function of their size', Phys. Rev. B, 2000, 62, (23), pp. 15942-15951
- [11] Harrison, P.: 'Quantum wells, wires and dots: theoretical and computational physics of semiconductor nanostructures' (John Wiley & Sons, 2005. 2005)
- [12] van Buuren, T., Dinh, L.N., Chase, L.L., Siekhaus, W.J., and Terminello, L.J.: 'Changes in the Electronic Properties of Si Nanocrystals as a Function of Particle Size', Phys. Rev. Lett., 1998, 80, (17), pp. 3803-3806
- [13] Iacona, F., Franzò, G., and Spinella, C.: 'Correlation between luminescence and structural properties of Si nanocrystals', J. Appl. Phys., 2000, 87, (3), pp. 1295-1303
- [14] Takagi, H., Ogawa, H., Yamazaki, Y., Ishizaki, A., and Nakagiri, T.:
   'Quantum size effects on photoluminescence in ultrafine Si particles', Appl. Phys. Lett., 1990, 56, (24), pp. 2379-2380
- [15] Boer, K.W., Poole, C.P., and Heremans, J.P.: 'Survey of semiconductor physics' (John Wiley & Sons New York, 2002. 2002)
- [16] Shockley, W., and Queisser, H.J.: 'Detailed balance limit of efficiency of p - n junction solar cells', J. Appl. Phys., 1961, 32, (3), pp. 510-519
- [17] Green, M.A., Emery, K., Hishikawa, Y., Warta, W., and Dunlop, E.D.:
   'Solar cell efficiency tables (version 46)', Progress in Photovoltaics: Research and Applications, 2015, 23, (7), pp. 805-812
- [18] Green, M.A.: 'Third generation photovoltaics: Ultra high conversion efficiency at low cost', Progress in Photovoltaics: Research and Applications, 2001, 9, (2), pp. 123-135
- [19] Perez-Wurfl, I., Hao, X., Gentle, A., Kim, D.H., Conibeer, G., and Green, M.A.: 'Si nanocrystal p-i-n diodes fabricated on quartz substrates for third generation solar cell applications', Appl. Phys. Lett., 2009, 95, (15), pp. 153506
- [20] Hao, X., Cho, E., Flynn, C., Shen, Y., Park, S., Conibeer, G., and Green, M.: 'Synthesis and characterization of boron-doped Si quantum dots for all-Si quantum dot tandem solar cells', Sol. Energy Mater. Sol. Cells, 2009, 93, pp. 273 - 279
- [21] Hao, X., Cho, E., Scardera, G., Shen, Y., Bellet-Amalric, E., Bellet, D., Conibeer, G., and Green, M.: 'Phosphorus-doped silicon quantum dots for all-silicon quantum dot tandem solar cells', Sol. Energy Mater. Sol. Cells, 2009, 93, pp. 1524 - 1530

- [22] Gnaser, H., Gutsch, S., Wahl, M., Schiller, R., Kopnarski, M., Hiller, D., and Zacharias, M.: 'Phosphorus doping of Si nanocrystals embedded in silicon oxynitride determined by atom probe tomography', J. Appl. Phys., 2014, 115, (3), pp. 034304
- [23] Stegner, A.R., Pereira, R.N., Lechner, R., Klein, K., Wiggers, H., Stutzmann, M., and Brandt, M.S.: 'Doping efficiency in freestanding silicon nanocrystals from the gas phase: Phosphorus incorporation and defect-induced compensation', Phys. Rev. B, 2009, 80, (16), pp. 165326
- [24] Simonds, B.J., Perez-Würfl, I., So, Y.-H., Wan, A.S., McMurray, S., and Taylor, P.C.: 'Phosphorous doping of superlattice silicon quantum dots in silicon dioxide', Phys. Status Solidi C, 2012, 9, (10-11), pp. 1908-1911
- [25] Lechner, R., Stegner, A.R., Pereira, R.N., Dietmueller, R., Brandt, M.S., Ebbers, A., Trocha, M., Wiggers, H., and Stutzmann, M.: 'Electronic properties of doped silicon nanocrystal films', J. Appl. Phys., 2008, 104, (5), pp. 053701
- Pi, X.D., Gresback, R., Liptak, R.W., Campbell, S.A., and Kortshagen, U.:
   'Doping efficiency, dopant location, and oxidation of Si nanocrystals', Appl. Phys. Lett., 2008, 92, (12), pp. 123102
- [27] Efros, A.L., and Rosen, M.: 'The Electronic Structure of Semiconductor Nanocrystals 1', Annual Review of Materials Science, 2000, 30, (1), pp. 475-521
- [28] Cantele, G., Degoli, E., Luppi, E., Magri, R., Ninno, D., Iadonisi, G., and Ossicini, S.: 'First-principles study of n- and p-doped silicon nanoclusters', Phys. Rev. B, 2005, 72, pp. 113303
- [29] Luo, X., Zhang, S.B., and Wei, S.-H.: 'Understanding Ultrahigh Doping: The Case of Boron in Silicon', Phys. Rev. Lett., 2003, 90, (2), pp. 026103
- [30] Cantele, G., Degoli, E., Luppi, E., Magri, R., Ninno, D., Iadonisi, G., and Ossicini, S.: 'First-principles study of n- and p-doped silicon nanoclusters', Phys. Rev. B, 2005, 72, (11), pp. 113303
- [31] Chan, T.L., Tiago, M.L., Kaxiras, E., and Chelikowsky, J.R.: 'Size Limits on Doping Phosphorus into Silicon Nanocrystals', Nano Lett., 2008, 8, (2), pp. 596-600
- [32] König, D., Gutsch, S., Gnaser, H., Wahl, M., Kopnarski, M., Göttlicher, J., Steininger, R., Zacharias, M., and Hiller, D.: 'Location and Electronic Nature of Phosphorus in the Si Nanocrystal – SiO<sub>2</sub> System', Sci. Rep., 2015, 5, pp. 9702
- [33] Gutsch, S., Laube, J., Hiller, D., Bock, W., Wahl, M., Kopnarski, M., Gnaser, H., Puthen-Veettil, B., and Zacharias, M.: 'Electronic properties of

phosphorus doped silicon nanocrystals embedded in SiO<sub>2</sub>', Appl. Phys. Lett., 2015, 106, (11), pp. 113103

- [34] Hao, X.J., Cho, E.C., Flynn, C., Shen, Y.S., Conibeer, G., and Green, M.A.: 'Effects of boron doping on the structural and optical properties of silicon nanocrystals in a silicon dioxide matrix', Nanotechnology, 2008, 19, (42), pp. 424019
- [35] Hao, X.J., Cho, E.C., Scardera, G., Bellet-Amalric, E., Bellet, D., Shen, Y.S., Huang, S., Huang, Y.D., Conibeer, G., and Green, M.A.: 'Effects of phosphorus doping on structural and optical properties of silicon nanocrystals in a SiO<sub>2</sub> matrix', Thin Solid Films, 2009, 517, (19), pp. 5646-5652
- [36] Antonova, I.V., Gulyaev, M., Savir, E., Jedrzejewski, J., and Balberg, I.:
   'Charge storage, photoluminescence, and cluster statistics in ensembles of Si quantum dots', Phys. Rev. B, 2008, 77, (12), pp. 125318
- [37] Gutsch, S., Laube, J., Hartel, A.M., Hiller, D., Zakharov, N., Werner, P., and Zacharias, M.: 'Charge transport in Si nanocrystal/SiO<sub>2</sub> superlattices', J. Appl. Phys., 2013, 113, (13), pp. 133703
- [38] Rose, A.: 'Space-Charge-Limited Currents in Solids', Phys. Rev., 1955, 97, (6), pp. 1538-1544
- [39] Puthen Veettil, B., Wu, L., Jia, X., Lin, Z., Zhang, T., Yang, T., Johnson, C., McCamey, D., Conibeer, G., and Perez-Würfl, I.: 'Passivation effects in B doped self-assembled Si nanocrystals', Appl. Phys. Lett., 2014, 105, (22), pp. 222108
- [40] Sarikov, A., Litovchenko, V., Lisovskyy, I., Maidanchuk, I., and Zlobin, S.: 'Role of oxygen migration in the kinetics of the phase separation of nonstoichiometric silicon oxide films during high-temperature annealing', Appl. Phys. Lett., 2007, 91, (13), pp. 133109
- [41] Shujuan, H., and Gavin, C.: 'Sputter-grown Si quantum dot nanostructures for tandem solar cells', J. Phys. D Appl. Phys., 2013, 46, (2), pp. 024003
- [42] Espiau de Lamaëstre, R., and Bernas, H.: 'Significance of lognormal nanocrystal size distributions', Phys. Rev. B, 2006, 73, (12), pp. 125317
- [43] Kourkoutis, L.F., Hao, X., Huang, S., Puthen-Veettil, B., Conibeer, G., Green, M.A., and Perez-Wurfl, I.: 'Three-dimensional imaging for precise structural control of Si quantum dot networks for all-Si solar cells', Nanoscale, 2013, 5, (16), pp. 7499-7504
- [44] Zacharias, M., Heitmann, J., Scholz, R., Kahler, U., Schmidt, M., and Bläsing, J.: 'Size-controlled highly luminescent silicon nanocrystals: A SiO/SiO<sub>2</sub> superlattice approach', Appl. Phys. Lett., 2002, 80, (4), pp. 661-663

- [45] López-Vidrier, J., Hernández, S., Hiller, D., Gutsch, S., López-Conesa, L., Estradé, S., Peiró, F., Zacharias, M., and Garrido, B.: 'Annealing temperature and barrier thickness effect on the structural and optical properties of silicon nanocrystals/SiO<sub>2</sub> superlattices', J. Appl. Phys., 2014, 116, (13), pp. 133505
- [46] Park, S.: 'Progress in All-Silicon Tandem Solar Cells with Silicon Quantum Dot in Silicon Dioxide Matrix', University of New South Wales, 2009
- [47] Kern, W.: 'Thin film processes II' (Academic press, 2012. 2012)
- [48] Seshan, K.: 'Handbook of thin film deposition' (William Andrew, 2012. 2012)
- [49] White, C.W., Wilson, S.R., Appleton, B.R., and Young, F.W.:
   'Supersaturated substitutional alloys formed by ion implantation and pulsed laser annealing of group - III and group - V dopants in silicon', J. Appl. Phys., 1980, 51, (1), pp. 738-749
- [50] Thompson, M.O., Galvin, G.J., Mayer, J.W., Peercy, P.S., Poate, J.M., Jacobson, D.C., Cullis, A.G., and Chew, N.G.: 'Melting Temperature and Explosive Crystallization of Amorphous Silicon during Pulsed Laser Irradiation', Phys. Rev. Lett., 1984, 52, (26), pp. 2360-2363
- [51] Shirk, M.D., and Molian, P.A.: 'A review of ultrashort pulsed laser ablation of materials', Journal of Laser Applications, 1998, 10, (1), pp. 18-28
- [52] Kachurin, G.A., Cherkova, S.G., Marin, D.V., Yankov, R.A., and Deutschmann, M.: 'Formation of light-emitting Si nanostructures in SiO<sub>2</sub> by pulsed anneals', Nanotechnology, 2008, 19, (35), pp. 355305
- [53] Pey, K.L., and Lee, P.S.: 'Pulsed laser annealing technology for nanoscale fabrication of silicon-based devices in semiconductors', in Pou, J., Low, D.K.Y., and Toyserkani, Advances in Laser Materials Processing (Woodhead Publishing, 2010), pp. 327-364
- [54] Young, R.T., White, C.W., Clark, G.J., Narayan, J., Christie, W.H., Murakami, M., King, P.W., and Kramer, S.D.: 'Laser annealing of boron - implanted silicon', Appl. Phys. Lett., 1978, 32, (3), pp. 139-141
- [55] Smith, B.C.: 'Fundamentals of Fourier transform infrared spectroscopy' (CRC press, 2011. 2011)
- [56] Lucovsky, G., and Pollard, W.B.: 'Local bonding of oxygen and hydrogen in a-Si:H:O thin films', Journal of Vacuum Science & Technology A, 1983, 1, (2), pp. 313-316

- [57] Viard, J., Beche, E., Perarnau, D., Berjoan, R., and Durand, J.: 'XPS and FTIR study of silicon oxynitride thin films', Journal of the European Ceramic Society, 1997, 17, (15–16), pp. 2025-2028
- [58] Zhang, T.: 'Fabrication and Characterization of Silicon Rich Oxide (SRO) Thin Film Deposited by Plasma Enhanced CVD for Si Quantum Dot', University of New South Wales, 2012
- [59] de Boer, W.D.A.M., Timmerman D., Dohnalova K., Yassievich, I.N., Zhang H., Buma, W.J., and Gregorkiewicz T.: 'Red spectral shift and enhanced quantum efficiency in phonon-free photoluminescence from silicon nanocrystals', Nat Nano, 2010, 5, (12), pp. 878-884
- [60] Khriachtchev, L., Räsänen, M., and Novikov, S.: 'Free-standing silica film containing Si nanocrystals: Photoluminescence, Raman scattering, optical waveguiding, and laser-induced thermal effects', Appl. Phys. Lett., 2005, 86, (14), pp. -
- [61] Mimura, A., Fujii, M., Hayashi, S., Kovalev, D., and Koch, F.: 'Photoluminescence and free-electron absorption in heavily phosphorusdoped Si nanocrystals', Phys. Rev. B, 2000, 62, (19), pp. 12625-12627
- [62] Langford, J.I., and Wilson, A.: 'Scherrer after sixty years: a survey and some new results in the determination of crystallite size', J. Appl. Crystallogr., 1978, 11, (2), pp. 102-113
- [63] Patterson, A.L.: 'The Scherrer Formula for X-Ray Particle Size Determination', Phys. Rev., 1939, 56, (10), pp. 978-982
- [64] Cho, E.-C., Green, M.A., Conibeer, G., Song, D., Cho, Y.-H., Scardera, G., Huang, S., Park, S., Hao, X., and Huang, Y.: 'Silicon quantum dots in a dielectric matrix for all-silicon tandem solar cells', Advances in OptoElectronics, 2007, 2007
- [65] Back, S.-H., Lee, G.-H., and Kang, S.: 'Effect of cryomilling on particle size and microstrain in a WC-Co alloy', Materials transactions, 2005, 46, (1), pp. 105-110
- [66] Hernández, S., Martínez, A., Pellegrino, P., Lebour, Y., Garrido, B., Jordana, E., and Fedeli, J.M.: 'Silicon nanocluster crystallization in SiO<sub>x</sub> films studied by Raman scattering', J. Appl. Phys., 2008, 104, (4), pp. 044304
- [67] Irmer, G.: 'Raman scattering of nanoporous semiconductors', Journal of Raman Spectroscopy, 2007, 38, (6), pp. 634-646
- [68] Hernández, S., López-Vidrier, J., López-Conesa, L., Hiller, D., Gutsch, S., Ibáñez, J., Estradé, S., Peiró, F., Zacharias, M., and Garrido, B.: 'Determining the crystalline degree of silicon nanoclusters/SiO<sub>2</sub> multilayers by Raman scattering', J. Appl. Phys., 2014, 115, (20), pp. 203504

- [69] Bustarret, E., Hachicha, M.A., and Brunel, M.: 'Experimental determination of the nanocrystalline volume fraction in silicon thin films from Raman spectroscopy', Appl. Phys. Lett., 1988, 52, (20), pp. 1675-1677
- [70] Felfer, P.J., Alam, T., Ringer, S.P., and Cairney, J.M.: 'A reproducible method for damage-free site-specific preparation of atom probe tips from interfaces', Microscopy Research and Technique, 2012, 75, (4), pp. 484-491
- [71] Fauchet, P.M.: 'Light emission from Si quantum dots', Materials Today, 2005, 8, (1), pp. 26-33
- [72] Conibeer, G., Perez-Wurfl, I., Hao, X., Di, D., and Lin, D.: 'Si solid-state quantum dot-based materials for tandem solar cells', Nanoscale Res. Lett., 2012, 7, (1), pp. 193
- [73] Cho, E., Park, S., Hao, X., Song, D., Conibeer, G., Park, S., and Green, M.:
   'Silicon quantum dot/crystalline silicon solar cells', Nanotechnology, 2008, 19, pp. 245201
- [74] Heitmann, J., Müller, F., Zacharias, M., and Gösele, U.: 'Silicon Nanocrystals: Size Matters', Advanced Materials, 2005, 17, (7), pp. 795-803
- [75] Boogaard, A., Roesthuis, R., Brunets, I., Aarnink, A.A.I., Kovalgin, A.Y., Holleman, J., Wolters, R.A.M., and Schmitz, J.: 'Deposition of High-Quality SiO<sub>2</sub> Insulating Films at Low Temperatures by means of Remote PECVD'. Proc. Proceedings of the 11th annual workshop on semiconductor advances for future electronics and sensors (SAFE 2008), Veldhoven, The Netherlands2008 pp. Pages
- [76] Ortiz, A., Lopez, S., Falcony, C., Farias, M., Cota-Araiza, L., and Soto, G.: 'Plasma enhanced chemical vapor deposition of SiO2 films at low temperatures using SiCl4 and O2', Journal of Electronic Materials, 19, (12), pp. 1411-1415
- [77] Reynes, B., and Bruyère, J.C.: 'High-density silicon nitride thin film in PECVD', Sensors and Actuators A: Physical, 1992, 32, (1–3), pp. 303-306
- [78] Iacona, F., Franzò, G., Irrera, A., Boninelli, S., and Priolo, F.: 'Structural and Optical Properties of Silicon Nanocrystals Synthesized': 'Silicon Nanocrystals' (Wiley-VCH Verlag GmbH & Co. KGaA, 2010), pp. 247-273
- [79] Carlsson, J.-O., and Martin, P.M.: 'Chapter 7 Chemical Vapor Deposition': 'Handbook of Deposition Technologies for Films and Coatings (Third Edition)' (William Andrew Publishing, 2010), pp. 314-363

- [80] Zhuo, Z., Sannomiya, Y., Kanetani, Y., Yamada, T., Ohmi, H., Kakiuchi, H., and Yasutake, K.: 'Interface properties of SiO(x)N(y) layer on Si prepared by atmospheric-pressure plasma oxidation-nitridation', Nanoscale Res. Lett., 2013, 8, (1), pp. 201-201
- [81] Denisse, C.M.M., Troost, K.Z., Oude Elferink, J.B., Habraken, F.H.P.M., van der Weg, W.F., and Hendriks, M.: 'Plasma - enhanced growth and composition of silicon oxynitride films', J. Appl. Phys., 1986, 60, (7), pp. 2536-2542
- [82] Lucovsky, G., Santos-Filho, P., Lu, Z., Jing, Z., and Whitten, J.L.: 'Bonding of oxygen and nitrogen atoms in hydrogenated amorphous silicon alloys', J. Non Cryst. Solids, 1995, 190, (1–2), pp. 169-179
- [83] Ay, F., and Aydinli, A.: 'Comparative investigation of hydrogen bonding in silicon based PECVD grown dielectrics for optical waveguides', Optical Materials, 2004, 26, (1), pp. 33-46
- [84] Pai, P.G., Chao, S.S., Takagi, Y., and Lucovsky, G.: 'Infrared spectroscopic study of SiO<sub>x</sub> films produced by plasma enhanced chemical vapor deposition', Journal of Vacuum Science & Technology A, 1986, 4, (3), pp. 689-694
- [85] Lucovsky, G., Yang, J., Chao, S.S., Tyler, J.E., and Czubatyj, W.:
   'Nitrogen-bonding environments in glow-discharge deposited a-Si:H films', Phys. Rev. B, 1983, 28, (6), pp. 3234-3240
- [86] Lucovsky, G., Nemanich, R.J., and Knights, J.C.: 'Structural interpretation of the vibrational spectra of a-Si: H alloys', Phys. Rev. B, 1979, 19, (4), pp. 2064-2073
- [87] Kirill O. Bugaev, A.A.Z., and Vladimir A. Volodin: 'Vibrational Spectroscopy of Chemical Species in Silicon and Silicon-Rich Nitride Thin Films', International Journal of Spectroscopy, 2012, 2012
- [88] Lanford, W.A., and Rand, M.J.: 'The hydrogen content of plasma deposited silicon nitride', J. Appl. Phys., 1978, 49, (4), pp. 2473-2477
- [89] Hussein, M.G., Wörhoff, K., Sengo, G., and Driessen, A.: 'Optimization of plasma-enhanced chemical vapor deposition silicon oxynitride layers for integrated optics applications', Thin Solid Films, 2007, 515, (7–8), pp. 3779-3786
- [90] Hernández, S., Miska, P., Grün, M., Estradé, S., Peiró, F., Garrido, B., Vergnat, M., and Pellegrino, P.: 'Tailoring the surface density of silicon nanocrystals embedded in SiOx single layers', J. Appl. Phys., 2013, 114, (23), pp. 233101

- [91] Hiller, D., Goetze, S., Munnik, F., Jivanescu, M., Gerlach, J.W., Vogt, J., Pippel, E., Zakharov, N., Stesmans, A., and Zacharias, M.: 'Nitrogen at the Si-nanocrystal interface and its influence on luminescence and interface defects', Phys. Rev. B, 2010, 82, (19), pp. 195401
- [92] Mulloni, V., Bellutti, P., and Vanzetti, L.: 'XPS and SIMS investigation on the role of nitrogen in Si nanocrystals formation', Surf Sci., 2005, 585, (3), pp. 137-143
- [93] Di, D., Perez-Wurfl, I., Conibeer, G., and Green, M.A.: 'Formation and photoluminescence of Si quantum dots in SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> hybrid matrix for all-Si tandem solar cells', Sol. Energy Mater. Sol. Cells, 2010, 94, (12), pp. 2238-2243
- [94] Lebour, Y., Pellegrino, P., Hernández, S., Martínez, A., Jordana, E., Fedeli, J.M., and Garrido, B.: 'Comparative study of Si precipitation in silicon-rich oxide films', Physica E: Low-dimensional Systems and Nanostructures, 2009, 41, (6), pp. 990-993
- [95] Dalba, G., Daldosso, N., Fornasini, P., Grisenti, R., Pavesi, L., Rocca, F., Franzò, G., Priolo, F., and Iacona, F.: 'Chemical composition and local structure of plasma enhanced chemical vapor-deposited Si nanodots and their embedding silica matrix', Appl. Phys. Lett., 2003, 82, (6), pp. 889-891
- [96] König, D., Hiller, D., Gutsch, S., and Zacharias, M.: 'Energy Offset Between Silicon Quantum Structures: Interface Impact of Embedding Dielectrics as Doping Alternative', Advanced Materials Interfaces, 2014, 1, (9), pp. n/a-n/a
- [97] Ehrhardt, F., Ferblantier, G., Muller, D., Ulhaq-Bouillet, C., Rinnert, H., and Slaoui, A.: 'Control of silicon nanoparticle size embedded in silicon oxynitride dielectric matrix', J. Appl. Phys., 2013, 114, (3), pp. 033528
- [98] Scardera, G., Puzzer, T., Perez-Wurfl, I., and Conibeer, G.: 'The effects of annealing temperature on the photoluminescence from silicon nitride multilayer structures', J. Cryst. Growth, 2008, 310, (15), pp. 3680-3684
- [99] König, D., Rudd, J., Green, M.A., and Conibeer, G.: 'Role of the interface for the electronic structure of Si quantum dots', Phys. Rev. B, 2008, 78, (3), pp. 035339
- [100] Moreno, J.A., Garrido, B., Pellegrino, P., Garcia, C., Arbiol, J., Morante, J.R., Marie, P., Gourbilleau, F., and Rizk, R.: 'Size dependence of refractive index of Si nanoclusters embedded in SiO2', J. Appl. Phys., 2005, 98, (1), pp. 013523
- [101] Gutsch, S., Hartel, A.M., Hiller, D., Zakharov, N., Werner, P., and Zacharias, M.: 'Doping efficiency of phosphorus doped silicon nanocrystals embedded in a SiO<sub>2</sub> matrix', Appl. Phys. Lett., 2012, 100, (23), pp. 233115

- [102] Zacharias, M., and Streitenberger, P.: 'Crystallization of amorphous superlattices in the limit of ultrathin films with oxide interfaces', Phys. Rev. B, 2000, 62, (12), pp. 8391-8396
- [103] Crowe, I.F., Halsall, M.P., Hulko, O., Knights, A.P., Gwilliam, R.M., Wojdak, M., and Kenyon, A.J.: 'Probing the phonon confinement in ultrasmall silicon nanocrystals reveals a size-dependent surface energy', J. Appl. Phys., 2011, 109, (8), pp. 083534
- [104] Hiller, D., Gutsch, S., Hartel, A.M., Löper, P., Gebel, T., and Zacharias, M.:
  'A low thermal impact annealing process for SiO<sub>2</sub>-embedded Si nanocrystals with optimized interface quality', J. Appl. Phys., 2014, 115, (13), pp. 134311
- [105] Xu, Q., Sharp, I., Yuan, C., Yi, D., Liao, C., Glaeser, A., Minor, A., Beeman, J., Ridgway, M., and Kluth, P.: 'Superheating and supercooling of Ge nanocrystals embedded in SiO<sub>2</sub>', Journal of Physics: Conference Series, (IOP Publishing, 2007, edn.), pp. 1042
- [106] Schneider, J.: 'Nucleation and growth during the formation of polycrystalline silicon thin films', PhD thesis, Technical University of Berlin, Fakultaet IV-Elektrotechnik und Informatik, 2005
- [107] Bonafos, C., Colombeau, B., Altibelli, A., Carrada, M., Ben Assayag, G., Garrido, B., López, M., Pérez-Rodríguez, A., Morante, J.R., and Claverie, A.: 'Kinetic study of group IV nanoparticles ion beam synthesized in SiO<sub>2</sub>', Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 2001, 178, (1–4), pp. 17-24
- [108] Tsoukalas, D., Tsamis, C., and Normand, P.: 'Diffusivity measurements of silicon in silicon dioxide layers using isotopically pure material', J. Appl. Phys., 2001, 89, (12), pp. 7809-7813
- [109] Rölver, R., Winkler, O., Först, M., Spangenberg, B., and Kurz, H.: 'Light emission from Si/SiO<sub>2</sub> superlattices fabricated by RPECVD', Microelectronics Reliability, 2005, 45, (5–6), pp. 915-918
- [110] Hiller, D., Goetze, S., and Zacharias, M.: 'Rapid thermal annealing of sizecontrolled Si nanocrystals: Dependence of interface defect density on thermal budget', J. Appl. Phys., 2011, 109, (5), pp. 054308
- [111] Aoyama, T., Tashiro, H., and Suzuki, K.: 'Diffusion of boron, phosphorus, arsenic, and antimony in thermally grown silicon dioxide', J. Electrochem. Soc., 1999, 146, (5), pp. 1879-1883
- [112] Dongaonkar, S., Servaites, J.D., Ford, G.M., Loser, S., Moore, J., Gelfand, R.M., Mohseni, H., Hillhouse, H.W., Agrawal, R., Ratner, M.A., Marks, T.J., Lundstrom, M.S., and Alam, M.A.: 'Universality of non-Ohmic shunt leakage in thin-film solar cells', J. Appl. Phys., 2010, 108, (12), pp. 124509

- [113] Pallarès, J., Cabré, R., Marsal, L.F., and Schropp, R.E.I.: 'A compact equivalent circuit for the dark current-voltage characteristics of nonideal solar cells', J. Appl. Phys., 2006, 100, (8), pp. 084513
- [114] Redfern, D., Musca, C.A., Dell, J.M., and Faraone, L.: 'Characterization of electrically active defects in photovoltaic detector arrays using laser beaminduced current', Electron Devices, IEEE Transactions on, 2005, 52, (10), pp. 2163-2174
- [115] Garnett, E.C., and Yang, P.: 'Silicon nanowire radial p- n junction solar cells', J. Am. Chem. Soc., 2008, 130, (29), pp. 9224-9225
- [116] Wu, L., Zhang, T., Lin, Z., Jia, X., Puthen-Veettil, B., Chien-Jen Yang, T., Xia, H., Conibeer, G., and Perez-Wurfl, I.: 'Silicon nanocrystal photovoltaic device fabricated via photolithography and its current–voltage temperature dependence', Sol. Energy Mater. Sol. Cells, 2014, 128, (0), pp. 435-440
- [117] Dalpian, G., and Chelikowsky, J.: 'Self-purification in semiconductor nanocrystals', Phys. Rev. Lett., 2006, 96, pp. 226802
- [118] Plummer, J.D.: 'Silicon VLSI Technology: Fundamentals, Practice, and Modeling' (Pearson Education, 2009. 2009)
- [119] Rossnagel, S.M., Cuomo, J.J., and Westwood, W.D.: 'Handbook of Plasma Processing Technology - Fundamentals, Etching, Deposition, and Surface Interactions', (William Andrew Publishing/Noyes, edn.), pp.
- [120] Golden, J., Miller, H., Nawrocki, D., and Ross, J.: 'Optimization of bi-layer lift-off resist process', CS Mantech Technical Digest, 2009
- [121] Fujii, M., Mimura, A., Hayashi, S., Yamamoto, Y., and Murakami, K.:
   'Hyperfine Structure of the Electron Spin Resonance of Phosphorus-Doped Si Nanocrystals', Phys. Rev. Lett., 2002, 89, (20), pp. 206805
- [122] Wen, X., Zeng, X., Zheng, W., Liao, W., and Feng, F.: 'Charging/discharging behavior and mechanism of silicon quantum dots embedded in amorphous silicon carbide films', J. Appl. Phys., 2015, 117, (2), pp. 024304
- [123] Park, N.-M., Choi, S.-H., and Park, S.-J.: 'Electron charging and discharging in amorphous silicon quantum dots embedded in silicon nitride', Appl. Phys. Lett., 2002, 81, (6), pp. 1092-1094
- [124] Shieh, J.-M., Huang, J.Y., Yu, W.-C., Huang, J.-D., Wang, Y.-C., Chen, C.-W., Wang, C.-K., Huang, W.-H., Cho, A.-T., Kuo, H.-C., Dai, B.-T., Yang, F.-L., and Pan, C.-L.: 'Nonvolatile memory with switching interfacial polar structures of nano Si-in-mesoporous silica', Appl. Phys. Lett., 2009, 95, (14), pp. 143501

- [125] Lin, D., Ma, L., Conibeer, G., and Perez-Wurfl, I.: 'Study on electrical properties of Si quantum dots based materials', Phys. Status Solidi B, 2011, 248, (2), pp. 472-476
- [126] Kachurin, G.A., Cherkova, S.G., Volodin, V.A., Marin, D.M., Tetel'baum, D.I., and Becker, H.: 'Effect of boron ion implantation and subsequent anneals on the properties of Si nanocrystals', Semiconductors, 2006, 40, (1), pp. 72-78
- [127] Hao, X., Podhorodecki, A., Shen, Y., Zatryb, G., Misiewicz, J., and Green, M.: 'Effects of Si-rich oxide layer stoichiometry on the structural and optical properties of Si QDs/SiO<sub>2</sub> multilayer film', Nanotechnology, 2009, 20, pp. 485703
- [128] Fujii, M., Hayashi, S., and Yamamoto, K.: 'Photoluminescence from Bdoped Si nanocrystals', J. Appl. Phys., 1998, 83, (12), pp. 7953-7957
- [129] Dalpian, G.M., and Chelikowsky, J.R.: 'Self-purification in Semiconductor Nanocrystals', Phys. Rev. Lett., 2006, 96, (22), pp. 226802
- [130] Schroder, D.K.: 'Carrier and Doping Density': 'Semiconductor Material and Device Characterization' (John Wiley & Sons, Inc., 2005), pp. 61-125
- [131] Hwang, Y., Engel-Herbert, R., Rudawski, N.G., and Stemmer, S.: 'Analysis of trap state densities at HfO2/In0.53Ga0.47As interfaces', Appl. Phys. Lett., 2010, 96, (10), pp. -
- [132] Peralagu, U., Povey, I.M., Carolan, P., Lin, J., Contreras-Guerrero, R., Droopad, R., Hurley, P.K., and Thayne, I.G.: 'Electrical and physical characterization of the Al<sub>2</sub>O<sub>3</sub>/p-GaSb interface for 1%, 5%, 10%, and 22% (NH<sub>4</sub>)<sub>2</sub>S surface treatments', Appl. Phys. Lett., 2014, 105, (16), pp. -
- [133] Kim, E.J., Wang, L., Asbeck, P.M., Saraswat, K.C., and McIntyre, P.C.: 'Border traps in Al<sub>2</sub>O<sub>3</sub>/In<sub>0.53</sub>Ga<sub>0.47</sub>As (100) gate stacks and their passivation by hydrogen anneals', Appl. Phys. Lett., 2010, 96, (1), pp. 012906
- [134] Jones, B.K., Sengouga, N., and Dehimi, L.: 'Relaxation semiconductor diodes: a practical review', Semiconductor Conference CAS 2000 Proceedings, 2000, pp. 323-326 vol.321
- [135] Schibli, E., and Milnes, A.G.: 'Effects of deep impurities on n+p junction reverse-biased small-signal capacitance', Solid-State Electron., 1968, 11, (3), pp. 323-334
- [136] Vogel, E.M., Richter, C.A., and Rennex, B.G.: 'A capacitance-voltage model for polysilicon-gated MOS devices including substrate quantization effects based on modification of the total semiconductor charge', Solid-State Electron., 2003, 47, (9), pp. 1589-1596

- [137] Sze, S.: 'Physics of Semiconductor Devices' (Wiley-Interscience, 1981. 1981)
- [138] Chan, T.L., Kwak, H., Eom, J.-H., Zhang, S.B., and Chelikowsky, J.R.:
   'Self-purification in Si nanocrystals: An energetics study', Phys. Rev. B, 2010, 82, (11), pp. 115421
- [139] Liedke, B., Heinig, K.-H., Mücklich, A., and Schmidt, B.: 'Formation and coarsening of sponge-like Si-SiO<sub>2</sub> nanocomposites', Appl. Phys. Lett., 2013, 103, (13), pp. 133106
- [140] Vick, G.L., and Whittle, K.M.: 'Solid Solubility and Diffusion Coefficients of Boron in Silicon', J. Electrochem. Soc., 1969, 116, (8), pp. 1142-1144
- [141] Pi, X., Chen, X., and Yang, D.: 'First-Principles Study of 2.2 nm Silicon Nanocrystals Doped with Boron', J. Phys. Chem. C, 2011, 115, (20), pp. 9838-9843
- [142] Brendel, R.: 'Appendix B: Recombination': 'Thin-Film Crystalline Silicon Solar Cells' (Wiley-VCH Verlag GmbH & Co. KGaA, 2005), pp. 209-239
- [143] Ma, L., Lin, D., Conibeer, G., and Perez-Wurfl, I.: 'Introducing dopants by diffusion to improve the conductivity of silicon quantum dot materials in 3rd generation photovoltaic devices', Phys. Status Solidi C, 2011, 8, (1), pp. 205-208
- [144] Stegner, A.R., Pereira, R.N., Klein, K., Lechner, R., Dietmueller, R., Brandt, M.S., Stutzmann, M., and Wiggers, H.: 'Electronic Transport in Phosphorus-Doped Silicon Nanocrystal Networks', Phys. Rev. Lett., 2008, 100, (2), pp. 026803
- [145] Kramer, N.J., Schramke, K.S., and Kortshagen, U.R.: 'Plasmonic Properties of Silicon Nanocrystals Doped with Boron and Phosphorus', Nano Lett., 2015, 15, (8), pp. 5597-5603
- [146] Nakamura, T., Adachi, S., Fujii, M., Miura, K., and Yamamoto, S.: 'Phosphorus and boron codoping of silicon nanocrystals by ion implantation: Photoluminescence properties', Phys. Rev. B, 2012, 85, (4), pp. 045441
- [147] Puthen Veettil, B., König, D., Patterson, R., Smyth, S., and Conibeer, G.:
   'Electronic confinement in modulation doped quantum dots', Appl. Phys. Lett., 2014, 104, (15), pp. 153102
- [148] So, Y.H., Huang, S., Conibeer, G., and Green, M.A.: 'N-type conductivity of nanostructured thin film composed of antimony-doped Si nanocrystals in silicon nitride matrix', EPL (Europhysics Letters), 2011, 96, (1), pp. 17011
- [149] Dalpian, G.M., and Chelikowsky, J.R.: 'Dalpian and Chelikowsky Reply', Phys. Rev. Lett., 2008, 100, (17), pp. 179703

- [150] Chong, Y.F., Pey, K.L., Wee, A.T.S., See, A., Chan, L., Lu, Y.F., Song, W.D., and Chua, L.H.: 'Annealing of ultrashallow p+/n junction by 248 nm excimer laser and rapid thermal processing with different preamorphization depths', Appl. Phys. Lett., 2000, 76, (22), pp. 3197-3199
- [151] Bin, Y., Yun, W., Haihong, W., Qi, X., Riccobene, C., Talwar, S., and Ming-Ren, L.: '70 nm MOSFET with ultra-shallow, abrupt, and superdoped S/D extension implemented by laser thermal process (LTP)', Electron Devices Meeting, IEEE, 1999, pp. 509-512
- [152] Whelan, S., Privitera, V., Italia, M., Mannino, G., Bongiorno, C., Spinella, C., Fortunato, G., Mariucci, L., Stanizzi, M., and Mittiga, A.: 'Redistribution and electrical activation of ultralow energy implanted boron in silicon following laser annealing', J Vac. Sci. Technol.B, 2002, 20, (2), pp. 644-649
- [153] Misra, N., Xu, L., Pan, Y., Cheung, N., and Grigoropoulos, C.P.: 'Excimer laser annealing of silicon nanowires', Appl. Phys. Lett., 2007, 90, (11), pp. 111111
- [154] Ingole, S., Aella, P., Manandhar, P., Chikkannanavar, S.B., Akhadov, E.A., Smith, D.J., and Picraux, S.T.: 'Ex situ doping of silicon nanowires with boron', J. Appl. Phys., 2008, 103, (10), pp. 104302
- [155] Zhang, T., Simonds, B., Nomoto, K., Puthen Veettil, B., Lin, Z., Perez Wurfl, I., and Conibeer, G.: 'Pulsed KrF excimer laser dopant activation in nanocrystal silicon in a silicon dioxide matrix', Appl. Phys. Lett., 2016, 108, (8), pp. 083103
- [156] Street, R.A.: 'Hydrogenated amorphous silicon' (Cambridge University Press, 2005. 2005)
- [157] Verburg, P.C., Römer, G.R.B.E., and Huis in 't Veld, A.J.: 'Twotemperature model for pulsed-laser-induced subsurface modifications in Si', Applied Physics A, 2013, 114, (4), pp. 1135-1143
- [158] Nettesheim, S., and Zenobi, R.: 'Pulsed laser heating of surfaces: nanosecond timescale temperature measurement using black body radiation', Chem. Phys. Lett., 1996, 255, (1–3), pp. 39-44
- [159] López-Vidrier, J., Berencén, Y., Hernández, S., Blázquez, O., Gutsch, S., Laube, J., Hiller, D., Löper, P., Schnabel, M., Janz, S., Zacharias, M., and Garrido, B.: 'Charge transport and electroluminescence of silicon nanocrystals/SiO2 superlattices', J. Appl. Phys., 2013, 114, (16), pp. 163701
- [160] Makise, K., Shinozaki, B., Asano, T., Mitsuishi, K., Yano, K., Inoue, K., and Nakamura, H.: 'Relationship between variable range hopping transport

and carrier density of amorphous  $In_2O_3-10$  wt. % ZnO thin films', J. Appl. Phys., 2012, 112, (3), pp. 033716

- [161] Qiu, H., Xu, T., Wang, Z., Ren, W., Nan, H., Ni, Z., Chen, Q., Yuan, S., Miao, F., Song, F., Long, G., Shi, Y., Sun, L., Wang, J., and Wang, X.: 'Hopping transport through defect-induced localized states in molybdenum disulphide', Nat Commun, 2013, 4
- [162] Mott, N.F., and Davis, E.A.: 'Electronic processes in non-crystalline materials' (Oxford University Press, 2012. 2012)
- [163] Morigaki, K.: 'Transport': 'Physics of Amorphous Semiconductors' (Imperial College Press, 1999)
- [164] McCluskey, M.D., and Haller, E.E.: 'Dopants and defects in semiconductors' (CRC Press, 2012. 2012)
- [165] Ghoshtagore, R.N.: 'Silicon dioxide masking of phosphorus diffusion in silicon', Solid-State Electron., 1975, 18, (5), pp. 399-406
- [166] Ghezzo, M., and Brown, D.M.: 'Diffusivity Summary of B, Ga, P, As, and Sb in SiO2', J. Electrochem. Soc., 1973, 120, (1), pp. 146-148
- [167] Schnabel, M., Weiss, C., Löper, P., Wilshaw, P.R., and Janz, S.: 'Selfassembled silicon nanocrystal arrays for photovoltaics', physica status solidi (a), 2015, 212, (8), pp. 1649-1661
- [168] Perez-Wurfl, I., Ma, L., Lin, D., Hao, X., Green, M.A., and Conibeer, G.:
   'Silicon nanocrystals in an oxide matrix for thin film solar cells with 492 mV open circuit voltage', Sol. Energy Mater. Sol. Cells, 2012, 100, pp. 65-68
- [169] Löper, P., Stüwe, D., Künle, M., Bivour, M., Reichel, C., Neubauer, R., Schnabel, M., Hermle, M., Eibl, O., Janz, S., Zacharias, M., and Glunz, S.W.: 'A Membrane Device for Substrate-Free Photovoltaic Characterization of Quantum Dot Based p-i-n Solar Cells', Advanced Materials, 2012, 24, (23), pp. 3124-3129
- [170] Choi, H., Nahm, C., Kim, J., Kim, C., Kang, S., Hwang, T., and Park, B.: 'Review paper: Toward highly efficient quantum-dot- and dye-sensitized solar cells', Current Applied Physics, 2013, 13, Supplement 2, pp. S2-S13
- [171] Nozik, A.J.: 'Quantum dot solar cells', Physica E: Low-dimensional Systems and Nanostructures, 2002, 14, (1–2), pp. 115-120
- [172] Houtepen, A.J., Kockmann, D., and Vanmaekelbergh, D.: 'Reappraisal of Variable-Range Hopping in Quantum-Dot Solids', Nano Lett., 2008, 8, (10), pp. 3516-3520

- [173] Wheeler, L.M., Neale, N.R., Chen, T., and Kortshagen, U.R.: 'Hypervalent surface interactions for colloidal stability and doping of silicon nanocrystals', Nat Commun, 2013, 4
- [174] Liu, X., and Swihart, M.T.: 'Heavily-doped colloidal semiconductor and metal oxide nanocrystals: an emerging new class of plasmonic nanomaterials', Chemical Society Reviews, 2014, 43, (11), pp. 3908-3920
- [175] Tondini, S., Pucker, G., and Pavesi, L.: 'Spectral- and time-resolved electroluminescence of silicon nanocrystals based light emitting devices', J. Phys. D Appl. Phys., 2015, 48, (45), pp. 455103
- [176] Walters, R.J., Bourianoff, G.I., and Atwater, H.A.: 'Field-effect electroluminescence in silicon nanocrystals', Nat Mater, 2005, 4, (2), pp. 143-146
- [177] Mazzitello, I.K., Mártin, O.H., and Roman, E.H.: 'Enhanced light emission in Si-nanoclusters arrays', The European Physical Journal B - Condensed Matter and Complex Systems, 2007, 54, (3), pp. 315-320