Final Year Project

Project Proposal

Photoluminescence and Band Gap Studies of Porous Silicon – Application to Solar Cells

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Project Summary

Although discovered in 1956, porous silicon gained little attention until the late 1980s when it was shown to possess interesting optical and electrical properties, most notably its efficient visible photoluminescence at room temperature. The electronic structure of porous silicon in the vicinity of its band gap is directly responsible for its photoluminescence properties. However, due to the inhomogeneous, fabrication-dependent nature of the material, the electronic structure exhibits inter-sample as well as intra-sample disparity, making it difficult to model and quantify. Therefore, the precise origin of porous silicon's photoluminescence remains unclear, although over 1500 papers have explored the issue.

Inexpensive, improved solar cell performance through use of porous silicon has been investigated due to its rough surface texture and high surface area-volume ratio which have advantages in reducing surface reflection and improving absorption of light, in addition to the width and adjustability of its band gap and efficacy as a gettering center for impurity atoms which enhance solar cell quantum efficiency. In this project, the band gap of porous silicon will be investigated through a review of available literature, development of a theoretical model and experimental measurements of the photoluminescence spectra of a porous silicon sample, which will be interpreted in the context of the model. The feasibility and advantages of the application of porous silicon to solar cell technology will be explored in light of this investigation.

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Introduction and Project Objectives

Crystalline silicon is a widely used and inexpensive material for solar cell applications. Its indirect band gap of 1.1 eV corresponds to emission in the infrared giving it a low emission efficiency of just 10^{-4} % [1] which restricts its use in optoelectronics. At the current time, where there is increasing demand for solar cell technology for power generation and consumer products, improvements in the efficiency of photovoltaic devices at low cost is of high importance. The optical, electrical, physical and chemical properties of porous silicon (PSi), different from those of crystalline silicon, are responsible for it gaining much attention in the field of optoelectronics, particularly its visible photoluminescence with quantum efficiency of up to 10% [11].

PSi layers are typically formed by electrochemical etching of crystalline silicon in aqueous hydrofluoric acid (HF) solution. This anodisation process typically results in a layer of micrometer depth consisting of a network of nanometer to micrometer sized silicon branches separated by pores of a similar size. The morphology, size and orientation of these pores and resulting silicon structures largely determines the optical and electronic properties of a sample of PSi and these physical properties depend upon the anodisation parameters as well as the properties of the silicon substrate. The effects of various fabrication parameters on the properties of the PSi layers are presented in Table 1. Silicon crystals with orientation <100> or <111> are used as PSi substrates because they are common sample orientations and produce pores that don't overlap or grow into each other.

Parameter increased	Effect on PSi properties
Si dopant type (n or p)	p: spongy PSi, n: linear pores [2]; larger pores from n-type [3]
Si dopant concentration	p: pore size/space increased, n: pore size/space decreased [3]
Si thickness	Increased average porosity, pore size distribution broadens [5]
Si resistivity	p: pore size decreases, n: pore size increases [5]
Si orientation	(100) wafer →square cross-sect,(111)→triangular cross-sect[5]
HF concentration	Decreased porosity [3]
Current density	Pore size increased [2],porosity increase [3],thickness increase [14]
Anodisation time	Increased porosity [3], increased thickness [15]
Illumination	Increased porosity (n-dope silicon samples) [5]

Table 1. The effect of increasing various etching parameters on the properties of PSi.

PSi is often distinguished by pore size through three classes as specified by IUPAC – microporous: $\leq$ 2nm, mesoporous: 2-50 nm and macroporous: > 50nm [5]. Pore examination is typically made by Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) at high resolution [5]. It has been experimentally identified that smaller pore sizes correlate with higher porosity PSi [9] and the optical properties PSi have been verified to have a dependence on the porosity of the sample. John et al [2] state that PSi with porosity greater than 60% exhibit visible luminescence, which can be attributed to the silicon crystallite size dependence of the photoluminescence properties [6]. Therefore, and since wholly microporous

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silicon requires highly concentrated HF solution, mesoporous silicon is the most extensively studied for luminescence investigations [5], and is type of PSi that will be used in experimental component of this project.

PSi possesses an interesting and heterogeneous electronic structure with a direct band gap, larger than that of crystalline silicon, due to vacancies, defects and a range of surface states, pore sizes and crystallite dimensions. It is the electronic structure of the material that determines its photoluminescence properties. However, the range of PSi properties between and within samples means that there is no single value for the band gap and calculating the precise electronic structure of a PSi sample is extremely difficult. The origin of an enhanced, direct band gap and the consequential visible luminescence of PSi was originally attributed to quantum confinement (QC) arising from the diminished dimensionality of the silicon structures [2,3], and it is regarded the most consistent model in explaining the experimental observations of the S-band photoluminescence of PSi [4]. QC is a phenomenon which becomes significant when the particle size is smaller than the exciton Bohr radius (analogy to the Hydrogen Bohr radius for electron-hole pairs), known as the strong confinement regime. In this case, the quantum 'particle in a box' model can be applied where the confinement energy is proportional to the inverse square of the particle ('box') size. From quantum theory, the permitted energies are given by,

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2 \tag{1}$$

for a particle confined in one-dimension, where n in the energy level, L is the size of the dimension (silicon nanostructure) and m is the reduced mass of the particle (which varies in the longitudinal and transverse directions for PSi). In QC theory, PSi containing silicon nanostructures smaller than the exciton Bohr radius will exhibit altered optical properties to bulk Si and the enhanced band gap will increase with decreasing nanostructure size. The confinement is also theorised to cause band gap folding resulting in the direct band gap from the indirect gap of bulk silicon [2]. Strong experimental evidence for this theory is supported by measurements of increased photoluminescence energy in PSi with decreased crystallite size [6].

In addition to the QC model, there are several other leading theories which attempt to explain the electronic structure and visible photoluminescence of PSi, including surface states, defects, hydrogenated amorphous silicon and siloxene (Si:H:O polymer) models [3, 5]. However, there is no current model which satisfies all experimental evidence and inflexible enough to be an unambiguous explanation of the properties of PSi [2]. A successful photoluminescence model will have a theoretical electronic band structure that supports the experimental evidence of the optical behaviour of PSi. Developing such a model based on investigation of the current leading models of PSi electronic structure and photoluminescence is a primary objective of this project.

Understanding the mechanism for visible photoluminescence and subsequently the electronic band structure of PSi is important to realising its potential applications to solar cells. PSi is of interest for solar cell applications primarily for its improved efficiency with respect to crystalline

silicon and relatively inexpensive production. PSi has a high surface area-to-volume ratio which enhances photon absorption and has a lower effective refractive index with respect to silicon which reduces its reflection to less than 5% over wavelengths 250 nm to 900 nm [7], thereby improving its external quantum efficiency. It has been shown to be effective as a sacrificial gettering centre for impurity atoms in multicrystalline and Czochralski-grown silicon solar cells [13,16] and surface passivation in oxidized PSi reduces the number of recombination centres that are associated with surface dangling bonds which increases the charge carrier lifetime in the cell, improving efficiency [8]. Crystalline silicon is relatively ineffective as a solar cell material because its direct band gap of 1.1eV is fixed and smaller than the theoretical solar cell efficiency-band gap peak of 1.5eV [16]. PSi, with a larger, direct band gap that is tunable across the whole visible range to the near UV and varied between and within samples [3,6] (a table of experimentally obtained values is given in Table 3, obtained from [6]), may be fabricated for optimal and broad light absorption and/or potentially to convert higher energy UV and blue photons into longer wavelengths in a tandem cell with silicon to improve its quantum efficiency [16]. Moreover, multiple layers of PSi with different band gaps may be used in thin film solar cells to absorb a wider spectrum of light [17] – the fundamental concept of thin-film solar cells, which are gaining interest as an efficient and inexpensive device. Understanding and being able to predict the band gap of PSi is integral to realising its potential in solar cell applications.

PL or EL* peak (eV)	FWHM (eV)	Excitation energy (eV)	Average bandgap (eV)	Method	Porosity	Substrate doping	Temp.
1.05	0.08	2.71	1.26	TR	53	p^+	4.2K
1.08	0.06	2.71	1.3	TR	64	p^+	4.2K
1.18	-	2.71	1.43	TR	78	p^+	4.2K
1.19	0.16	1.96	-	-	-	p^+	15K
1.4	0.25	-	1.63	EC	80	p^-	RT
1.55	0.38	2.5	1.78	PLE	-	p^-	RT
1.55	0.31	2.33	1.82	X	-	p^-	RT
1.6	0.25	-	1.95	EC	80	p^-	RT
1.62	-	-	1.8	PC	-	p^-	RT
1.81	0.46	3.81	-	-	-	p^-	RT
2	-	-	2.1	PN	-	-	RT
2.27	0.38	3.81	-	-	-	p^-	RT
2.34	-	-	-	-	-	p^-	RT
3.1	-	3.81	-	-	-	p^-	RT

Table 3. Measured PSi band gaps for a variety of samples along with particular parameters [6].
*PL is photoluminescence and EL is electroluminescence.

Research and Modeling Plan

This project initially requires an extensive literature review which will form a context and provide necessary theoretical tools for the development of a photoluminescence model that will

be verified through experimental testing of PSi samples, if time permits. These investigations and experimental observations will be interpreted in the context of solar cell applications.

Literature Review

An extensive literature review will be undertaken spanning topics from the fundamentals of solid state and semiconductor physics to state-of-the-art developments in porous semiconductor technology and photoluminescence and band gap models of PSi. Background knowledge in the relevant fields will be gain from textbooks, lecture notes and eBooks. With this knowledge, a range of journal articles will be critically read in conjunction with review papers, eg. *Datareviews*, regarding PSi. Specific focus will be given to photoluminescence and electronic band gap studies and the application of PSi to solar cells. Since the optical properties of PSi is a relatively new field of study, conference abstracts and papers will be highly useful, particularly those from the 2012 conference on porous semiconductor science and technology.
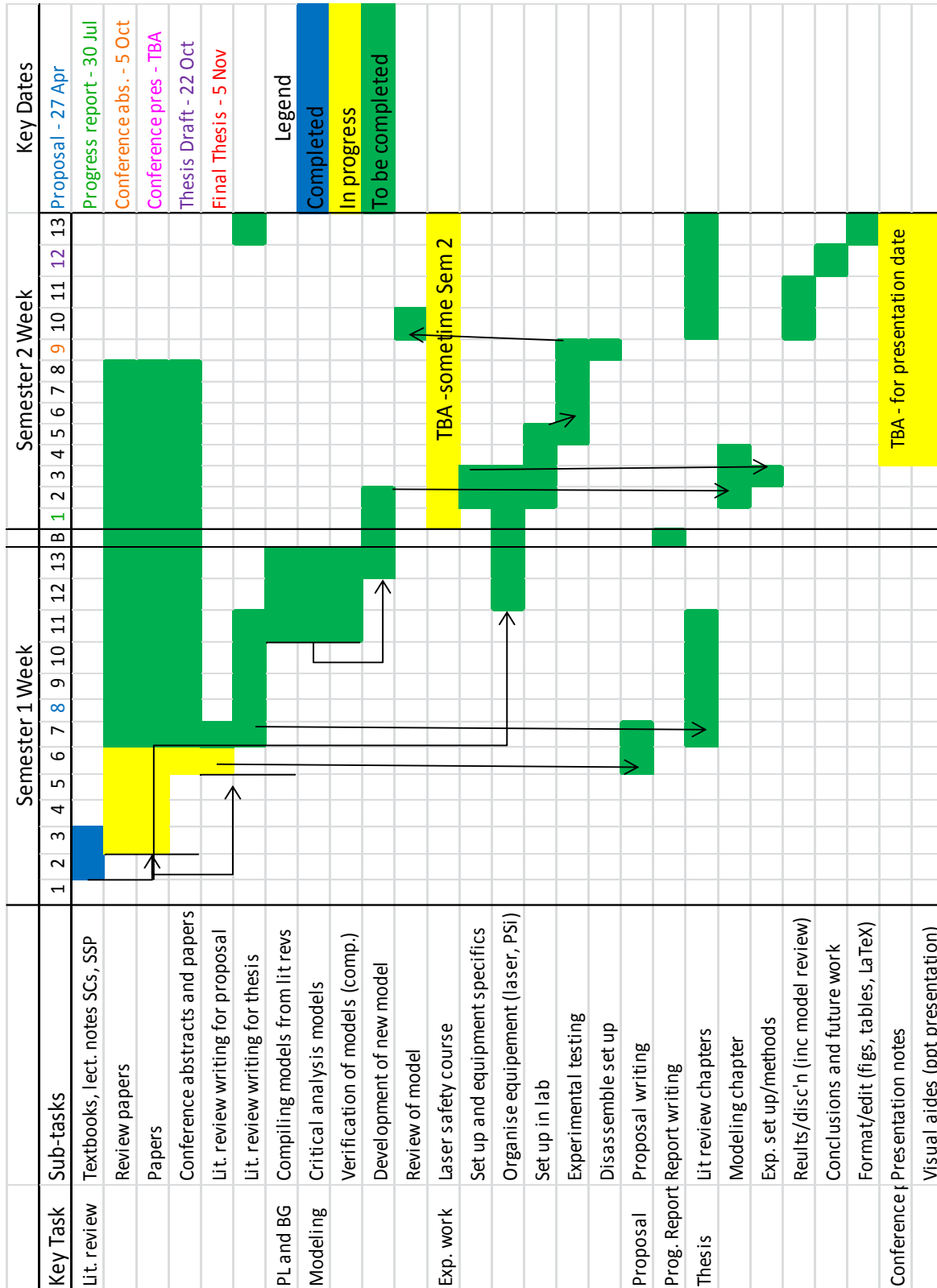
Modeling

Modeling of the electronic band gaps of PSi will be based on recent theoretical studies and experimental evidence of its electronic and optical properties. Current theoretical models will be critically analysed and interpreted in order to develop a new model. Verification of current models and new model development will be done using computing software, Matlab and/or Mathematica. These models will constantly be modified throughout the project as new ideas are conjured and derived from the continual literature review.

Experimental

The band gap of samples of mesoporous Si will be studies through photoluminescence measurements with a spectrometer in the UWA Optics Laboratory or Electrical Engineering Department, if time permits. The sample will be excited with a blue laser (360-480 nm emission), bought prior to the commencement of experimental work. The samples will be oxidized <100> mesoporous silicon formed on p-type silicon. This type of PSi is selected due to its adequately small silicon crystallite sizes to improve the likelihood of it exhibiting visible photoluminescence due to its relatively large band gap (relevant in the context of solar cell applications), in addition to its multitude of previous studies [5]. Furthermore, microporous silicon, requiring very high concentrations of HF [2], is impractical for this project. The <100> orientation is selected because PSi is usually grown on <100> silicon wafers which preferentially generates this pore orientation and is most common in previous studies [6]. Oxidation of the sample is preferred because it is likely that the pore size of the mesoporous silicon will not be precisely known and therefore it may not visibly photoluminesce at room temperature. However, oxide growth has been demonstrated to significantly narrow the pore size of PSi [12], supported experimentally be an observed blue shift in the PSi photoluminescence peak after natural oxidation [10]. Furthermore, photoluminescence properties of fresh PSi have been shown to degrade significantly with time, however this degradation is absent for oxidized PSi [3].

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Project Timeline

Semester 1 Week: 1 2 3 4 5 6 7 8 9 10 11 12 13 B
Semester 2 Week: 1 2 3 4 5 6 7 8 9 10 11 12 13

Key Task	Sub-tasks
Lit. review	Textbooks, lect. notes SCs, SSP
	Review papers
	Papers
	Conference abstracts and papers
	Lit. review writing for proposal
	Lit. review writing for thesis
PL and BG	Compiling models from lit revs
Modeling	Critical analysis models
	Verification of models (comp.)
	Development of new model
	Review of model
Exp. work	Laser safety course
	Set up and equipment specifics
	Organise equipement (laser, PSi)
	Set up in lab
	Experimental testing
	Disassemble set up
Proposal	Proposal writing
Prog. Report	Report writing
Thesis	Lit review chapters
	Modeling chapter
	Exp. set up/methods
	Reults/disc'n (inc model review)
	Conclusions and future work
	Format/edit (figs, tables, LaTeX)
Conference p	Presentation notes
	Visual aides (ppt presentation)

Chart annotations:
- TBA - sometime Sem 2
- TBA - for presentation date

Key Dates

- Proposal - 27 Apr
- Progress report - 30 Jul
- Conference abs. - 5 Oct
- Conference pres - TBA
- Thesis Draft - 22 Oct
- Final Thesis - 5 Nov

Legend

- Completed
- In progress
- To be completed

Risk Management

Risk Class	Description of risk	Likelihood	Consequences	Management Strategy
Safety	Laser – eye damage possible if looked directly into.	Possible	Moderate-major (depends on laser class)	Attend Laser Safety Course (Sem 2) and complete online module.
Environmental	No significant risk.	-	-	-
Financial	Require purchase of an expensive laser.	Unlikely	Moderate	Begin looking for suitable laser early, if unable to get an inexpensive one, resort to DVD-grade laser.
Project Outcomes	PSi sample does not visibly photoluminesce as a result of its physical properties.	Unlikely	Moderate	Use oxidised PSi samples since they exhibit blue shifted luminescence from fresh PSi. May be possible to obtain another sample if one does not visibly photoluminescence.
	PSi sample does not display visible photoluminescence as a result of experimental errors.	Possible	Major	Research and plan experimental set up and methods thoroughly prior to undertaking it. Carefully set up and ask supervisor for assistance if required.
	Optics laboratory unavailable when intended to be used for experimental work.	Possible	Minor	Book laboratory well in advance or ensure that nobody else is intending to use it during the desired period.
	Inability to source an adequate blue laser for experimental work.	Unlikely	Major	Seek laser early on ensure a back-up option such as a DVD-grade blue laser is viable.
	Laser malfunctions (eg. 'blows up')	Possible	Moderate	Attend laser safety course, complete online laser safety module and carry out induction to lab to ensure understanding of equipment operation.
	Loss of work due to computer failure	Unlikely	Major	Regularly save work to multiple places throughout project.

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[14] Luna Lopez J A, Chaires Villalba J, Carrillo Lopez J, Garcia Salgado G, Gomez Barojas E and Flores Garcia F J, *Optical and electrical properties of the porous silicon layers,* Porous Semiconductors – Science and Technology Conference, Malaga, Spain, 2012, Abstract P1-18

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[17] Basitde S, Nychyporuk T, Fave A and Lemiti L, *Metal assisted chemical etching of silicon-based dielectrics*, 2012, Porous Semiconductors – Science and Technology Conference, Malaga, Spain, 2012, Abstract O1-02

Appendix A – Induction Form

On the advice of my supervisor, Prof Adrian Keating, the induction forms need not be completed at the current time. Should any experimental work be carried out, the requisite induction forms will be completed prior to the commencement of laboratory work.

Appendix B – Risk parameters

Likelihood	Description
Probable	The event is expected to occur within the time frame of the project
Possible	The event is not expected to occur in the time frame of the project
Improbable	Conceivable but highly unlikely to occur during the project
Consequence	**Description**
Severe	Most objectives cannot be achieved
Major	Some important objectives cannot be achieved
Moderate	Some objectives affected
Minor	Minor effects that are easily remedied
Negligible	Negligible impact on objectives

Guidelines for classifying the likelihood and consequences of risk factors. (Based on HB 436:2004 Risk Management Guidelines – companion to Australian Standard AS/NZ 4360:2004)