Project Proposal

Study of the Effect of Thermal Annealing on the Properties of Porous Silicon

20503092, Matthew Ricciardo
School of Mechanical and Chemical Engineering,
University of Western Australia

Supervisor

Adrian Keating
School of Mechanical and Chemical Engineering,
University of Western Australia

Submitted: 26th April 2012
**Project Summary**

This project aims to explore the effects of thermal annealing on porous silicon to help understand the mechanisms behind the thermal nitridation passivation method and possibly explain some abnormalities noted by current studies conducted at the University of Western Australia. This will involve the study of literature and compilation of previously recorded experiments, which will be accompanied by finite element modelling of the currently used rapid thermal annealing method with ANSYS. Analysis of the gas flows within the annealing chamber will be conducted to explore the theory that interactions between the flow of nitrogen gas over the porous silicon surface and the evolved hydrogen gas are producing an uneven passivation layer. At the moment, reasons for the non-uniform surface passivation and details of the processes taking place during thermal annealing are relatively unknown; hence this project aims to improve the current understanding of the field.
Introduction and Project Objectives

The main objective of this project is to study the effects of thermal annealing on the properties of Porous Silicon (PS), with a particular focus on surface passivation. Porous Silicon is largely used in the field of optoelectronics and for sensor applications; hence a predictable and stabilised surface layer is required. Porous Silicon typically has a large specific surface area, ranging from ~200 to 600 m$^2$/cm$^3$ (Canham 1997), therefore is susceptible to room temperature oxidation. Studies have shown that low temperature rapid thermal annealing (RTA) of PS in a nitrogen rich environment can create surface passivation, however the exact mechanisms for this process are still unknown (James et al. 2009). It has also been noted in subsequent work that there is a lack of uniformity of the passivation layer, which must also be explored so that a larger portion of the fabricated PS can be utilised for component manufacturing.

Porous Silicon was accidentally discovered in 1956 by Arthur Uhlir at Bell Labs while working of chemical methods to improve the surface of silicon and germanium single crystals. The scientific community's interest in PS however remained relatively low until 1990, when the room temperature photoluminescence of PS was discovered by Canham. This would appear to be the key event which triggered a dramatic increase (exponentially) in the number of publications on PS and its properties (Parkhutik 2000).

The noted discovery of photoluminescence may have started the interest in PS, but its other unique properties such as tuneable refractive index and large specific surface area have ensured continued studies into its production methods and applications. Porous Silicon is most commonly produced using electrochemical anodisation due to the greater control over porosity and uniformity than electroless methods. This method involves a silicon wafer being submerged in a HF solution and subjected to an external electric current, which effectively results in the hydrogen atoms on the H-terminated silicon to be replaced by fluorine atoms that are then chemically removed as SiF$_4$ from the surface of the bulk structure. Left behind are voids where the Si atoms were removed and the surrounding Si structure will remain H-terminated, this is typically called as-fabricated PS.

As-fabricated PS is extremely reactive and readily oxidises in ambient conditions due to its large specific surface area. This can be detrimental to its optical properties and restrict possible applications unless it is treated with a passivation method to stabilise the surface.
Porous silicon is often passivated by a technique called thermal nitridation which involves the annealing of the as-fabricated PS in a nitrogen rich (or ammonium) atmosphere, in most cases this is conducted at high temperatures (in excess of 1000°C) with the exception of work done by James et al. (2009). Temperatures as low as 520°C were recorded to yield suitable surface passivation, which is preferential to previous methods as higher annealing temperatures tend to degrade the properties of PS and can result in sintering and unwanted modification to the porous structure. This low temperature nitrogen based technique uses rapid thermal annealing with ramp rates of 20°C/s to achieve passivation in a relatively short period of time and with negligible effects to the optical properties.

Further studies on low temperature nitrogen based annealing of PS at the University of Western Australia have shown that the passivated film is not uniform across the entire PS surface, hence only a small proportion of the sample can be utilised. Reasons for these observations are currently unknown; however some theories have been presented. It was initially thought to be the result of non-uniform temperature distribution within the annealing chamber, but a more prevalent theory is that there is an interaction between the gas flows. More specifically the flow of nitrogen gas over the PS surface may be altered by the hydrogen gas desorbing from the sample, resulting in an uneven distribution of nitrogen over the surface and thereby producing varying levels of passivation.

As it currently stands only a relatively small portion of the passivated PS produced, using the current nitrogen based RTA methods, can actually be utilised for the fabrication of sensor components due to the lack of uniformity in the passivation coating. Various theories have been presented as possible explanations, some of which will be explored in this project to further understand the processes occurring during thermal annealing and the changes to the PS properties.
Research & Model Development

This project can effectively be split into two key task groups; 1. Compile and review the current understanding of PS annealing processes, theories, and chemical interactions, and 2. Model the thermal annealing method currently used to explore the interactions (thermal, structural, and gas flow) which occur within the processing chamber. By combining the results of these two key task groups it should be possible verify the modelled data against previous literature and gain a better understanding of the annealing mechanisms.

Initial research began with a focus on the general properties and uses of PS to gain a basic understanding of the material and its unique properties. The common production methods were then explored to build a foundation understanding which leads into the study of PS thermal annealing procedures. The annealing of PS is conducted primarily to passivate the material; hence a major component of the research will include the passivation method and explore the chemical reactions occurring. This will involve the collection of experimental data from previous literature and a comparison between the techniques used and observed results. This will mostly focus on the different forms of the nitridation process as current work at the University of Western Australia is in this field, but a brief review of other passivation methods (such as oxidation and carbonisation) will also be conducted as a comparison.

The chemical and physical reactions occurring within the annealing chamber are of particular importance, hence a review of the hydrogen desorption process will be conducted. The findings from this will be especially important during later modelling processes as details of hydrogen evolution from the PS surface will be required to accurately represent the gas flows.

To model the thermal annealing process details of the equipment being used and sample treatment times will be required. Preliminary modelling of the AS-One 100 RTP (rapid thermal processor) was conducted by Gupta (2010), however the results were not conclusive. Specific data for the RTP's characteristics (most likely sourced from the manufacturer or previous testing) will be required for input into modelling software.

Initial modelling will be conducted using ANSYS to analyse the structural and thermal properties during annealing. Solid models of components will be produced directly within ANSYS and not imported from other modelling software (i.e. Solidworks) to reduce the risk of incompatibilities between software packages. The results from thermal and structural
modelling will be verified against literature, with one example being the 'Thermal modelling of RTP and RTCVD processes' by Kersch and Schafbauer (2000). Verified results will then be fed back into the software and used for the modelling of gas flows within the annealing chamber.

The analysis of gas flows will be modelled using ANSYS FLUENT and/or ANSYS CFD, however due to a lack of experience with finite element fluid modelling techniques these must first be learnt and applied through the use of online guides and examples. If time permits other modelling software may be identified and used to verify the results, but past literature will be the primary source for model verification.

**Project Timeline**

This project has been broken down into two major parts; the first being primarily an extensive literature review of reported PS annealing methods which will be conducted mostly during the first half of 2012, and the finite element modelling of the RTP which should begin by early June. The key tasks and expected dates will be discussed here, while a detailed Gantt chart can be found in the appendices.

General background research has been conducted from early March until the present, although it has not been extended on the Gantt chart, it will most likely continue as the need arises. A review of nitridation as a passivation method has been ongoing for the last month and should conclude with a comparison with other passivation methods by late May. This will be accompanied by research into hydrogen desorption and a review of RTP methods in early May, which should provide sufficient data to begin the modelling process.

Initial modelling should begin in early June, after becoming familiar with the ANSYS software package and fluid flow analysis techniques throughout April and May. The modelling process has been split into separate tasks as seen in the Gantt chart, and extra time allowed for verification and remodelling if necessary during early September. By late September the results from modelling should be finalised and verified against literature.

Early October has been set aside for finalising any unfinished work and tying together the literature review with modelling results. Note that research tasks and the review of literature
will continue throughout the course of this project; however this outline has focussed on the background research required to understand the fundamentals and begin the modelling.

**Risk Management**
Due to the nature of this project being primarily theoretical there are very little risks involved, however this risk assessment will be broken down into the required subsections as follows.

**Safety**
There are virtually no perceivable risks to a person(s) safety as a result of this project as the work is essentially theoretical, and consists of computer modelling with no plans for experimental work.

**Environmental**
There will also be no significant environmental risks associated with this project due to the non-physical nature of the task.

**Financial**
The financial risk of this project could also be considered negligible as modelling will be conducted using software which is already available, and verification can be done against results found in literature. Note that there should not be any need to organise experimental test for comparison as part of this project, as similar work is already being conducted at the University of Western Australia which can be used to verify findings without incurring further financial expenses.

**Project Outcomes**
Most risks associated with this project would fall into this category, which includes events that may prevent the project from being completed or achieving the desired outcomes. Due to this project's focus on modelling, the security and accessibility of data generated will be of high importance. It is possible for data to be lost as the result of equipment failure or loss of storage device, which would have major consequences and may set the project back many weeks depending on the content of the data. Therefore all documents and modelling data generated during this project will be stored on Dropbox, with regular backup copies made to external media. There is also a reliance on access to ANSYS modelling software and as such actions have already been taken to get off-site access from a personal laptop.
# Final Year Project Proposal, Semester 1, 2012

## Appendix

Gantt chart – Project Timeline
References


Gupta, R 2010, Effect of thermal annealing on the properties of porous silicon, School of Mechanical Engineering, The University of Western Australia.

