Australian Government
Australian Renewable Energy Agency

ARENA

Metal assisted chemical etching of SLIVERs

Project results and lessons learnt

Lead organisation:	The Australian National University
Project commencement date: 11/03/2013	**Completion date:** 11/09/2018
Date published:	
Contact name:	Katherine Booker
Title:	Dr
Email: Katherine.booker@anu.edu.au	**Phone:** 02 6125 8539
Website:	

Table of Contents

Executive Summary

The project involved the groove etching of SLIVER solar cells using a metal-assisted etch (MAE) of silicon (Si) wafers. SLIVER solar cells are the product of a pioneering project at the Australian National University by Prof. Andrew Blakers and Ass.Prof Klaus Weber. A SLIVER solar cell is a cell that is manufactured through the micromachining of narrow, deep grooves along a Si wafer surface (see diagram) to produce a solar cell that is narrow, thin, bifacial and flexible.

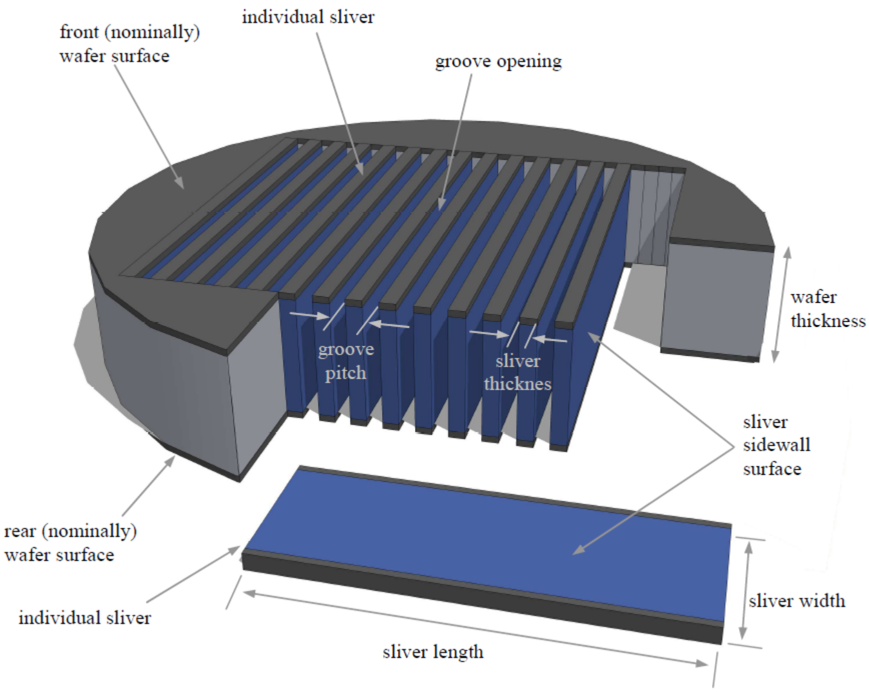

Figure 1. SLIVER solar cell design.

Metal assisted etching of Si wafers is a technique which has become a commonly-used practice in both research and industry for Si wafer texturing. The process is based on a localised oxidation and etch reaction, catalysed by metal deposited on the Si surface.

MAE is predominantly used for nano-scale etching of surface features, with only a few examples in the literature of etching larger (micron-scale) features or groove-type architectures. MAE etching of SLIVER grooves represents a novel application of the technology and can improve on current SLIVER manufacturing methods. The fact that MAE is not reliant on crystal orientation means that:

- <100> Si wafers can be used as starting material in place of the significantly more expensive <110> wafers,
- Grooves can be etched in any direction to make any shape which will greatly enhance wafer utilisation and broaden potential applications of the technology; and

- Texturing can be conducted in-situ during groove formation. This would greatly reduce the number of processing steps required to produce a textured SLIVER.

This project demonstrated that MAE can be used to etch 10-30µm-wide features (including spiral features) through a 650µm-thick wafer, although there are still some outstanding issues with the completeness of the etch i.e. some unetched sections of Si remain in the groove post-etching. Wafer utilisation was improved from 81% for a conventional SLIVER etching structure to a potential 95% using a spiral shape. Importantly, it was also shown that the metal could be successfully removed post-etching to avoid any sample contamination. Modelling studies on various surface features identified patterns which can be included in the SLIVER design in order to optimise light-trapping. Results show that current gains of 3.7% can potentially be achieved compared to the non-textured SLIVER equivalent.

Project Overview

Project summary

MAE was used as a method to groove etch SLIVER solar cells. The MAE method can circumvent the need to use expensive, custom-made <110> Si wafers as well as increase the wafer utilisation by etching the SLIVERs in any orientation to make use of the entire Si wafer. The ability to remove metal contaminants from the Si post-etching, as well as the effectiveness of various texture patterns on the SLIVER surface was also investigated.

Project scope

The project involved a thorough investigation of the MAE process as it applies to etching SLIVER grooves. This included testing a range of system parameters such as the properties of the metal catalyst, the effects of pre- and post-treatment of the Si wafer and the etching conditions. Of particular consideration was the effect of the Au layer thickness as this can potentially affect the mechanics of the etching system as well as contribute to overall stability/reproducibility of the etch. Once the SLIVER has been etched, another important consideration is that of metal removal. Any residual Au in or on the wafer may cause contamination at later processing stages. A method for Au removal was developed and the Si tested for Au contamination issues.

The manufacture of novel geometric shapes was considered. As well as allowing for the customisation of solar cells for certain applications, this also enables wafer utilisation to be considerably enhanced. Due to the crystallographic dependence of the conventional SLIVER etch regime, it is only possible to etch the SLIVERs in straight lines across the Si wafer. Given that wafers are circular in nature, there is a significant amount of Si wastage. Etching in a circular or spiral pattern allows more of the Si to be turned into a working solar cell. The project demonstrates the ability of the MAE technique to produce these kinds of structures.

Texturing plays an important part in enhancing the light absorption of the SLIVER cell. The texturing method currently employed for SLIVER wafers is time consuming and involves additional processing steps. MAE allows texturing to be achieved in-situ, as the SLIVER is being grooved, simply by grooving a sawtooth or waveform pattern rather than a straight line.

Outcomes

SLIVER groove etching

MAE was used to etch SLIVER grooves through a 650µm-thick wafer with groove widths of 10-30µm. It was shown that etching with a thicker Au layer improved the stability and reproducibility of the etch, however this required heat treatment of the Au layer to induce porosity. The balance between Au thickness and porosity was difficult to achieve but is a critical factor in producing deep and regular SLIVER grooves. If the Au layer is too thin or fragile, it will fracture during the etching process, leading to sections of unetched Si in the SLIVER groove. The Au layer was also shown to increase in porosity during the etching process. This makes control over the process very challenging, however, some parameters were identified (Au thickness, heat treatment to induce porosity) which help to control the regularity of the process. Etching in any direction was demonstrated by etching the wafers in a spiral pattern (see Figure 2). This also demonstrates the ability of the MAE method to significantly improve wafer utilisation. Wafer utilisation of >95% is possible using this method. This improves on the industry utilisation for SLIVER wafers of ~81%.

Figure 2. A spiral SLIVER section

Metal contamination removal

After the completion of groove etching, SLIVER wafers were subjected to an acidic etch solution to dissolve any Au particles. Analysis of samples after a subsequent high temperature process step of the SLIVERs demonstrated no degradation of the SLIVER had occurred, signifying that the Au had been successfully removed.

Texturing design

Modelling of various surface patterns for SLIVER wafers established the general trends in terms of texture design that need to be followed to maximise the light trapping in the SLIVER, as well as make the most use of the available Si. It was shown that the total SLIVER thickness needed to remain constant for there to be significant gains in terms of current output/Si wafer i.e. while large feature patterns increase the light trapping in the SLIVER, the amount of wasted Si leads to an overall reduction in total current/Si wafer. Small feature sizes with back-side feature angles >60° were identified as the most promising designs for future synthesis and total current gains of 3.7% per SLIVER wafer are predicted.

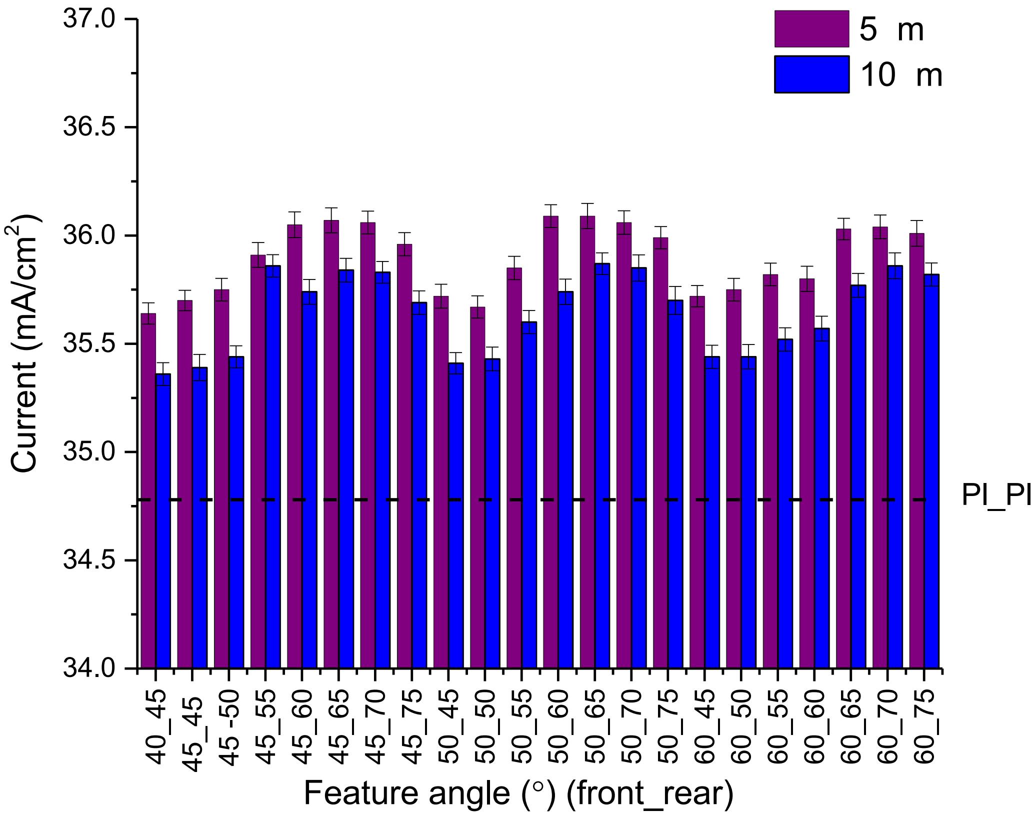

Figure 3. Predicted current output for SLIVERs with 5µm and 10µm-high surface features with various front and rear angles. The dashed lines represents a SLIVER with planar front and rear.

Transferability

The outcomes of the MAE studies are applicable not only to SLIVER processes but may also be useful for texturing studies involving Au thin films as the behaviour of the films and the effects of many different experimental parameters have been investigated in detail.

The techniques developed here are relevant for other projects where rounded or flexible features are desired. It can be applied to create solar cells with a curved profile or one where the call can be wrapped around an object, feature of a building etc. The fact that MAE can be used to etch deep features with any shape may find application in more general Si processing such as the creation of through-vias for microelectronics or possibly as a wafering technique.

The outcomes of the modelling study can be used as the basis for future SLIVER-based process which can conduct patterning and etching based on the structures identified as the best for light trapping. The results may also be of interest to other solar cells projects involving very thin solar cells. The effects on light trapping of the various structures on front and rear as well as the impact of cell thickness will hold broad interest.

Publications

Booker, K., et al. (2014). "Metal-assisted chemical etching for very high aspect ratio grooves in n - type silicon wafers." Journal of Micromechanics and Microengineering **24**(12): 125026

Manuscript in conference proceedings EUPVSEC 2014 – "Metal assisted etching of SLIVER solar cells".

Booker, K., et al. (2016). "Metal-assisted etching of high aspect ratio structures for solar cell applications: Controlling the porosity of Au thin films." IEEE Journal of Photovoltaics **6** (2): 393-396

Manuscript in conference proceedings PVSC42 2015 – "Metal-assisted etching of high aspect ratio structures for solar cell applications: Controlling the porosity of Au thin films."

Intellectual Property: Patents / Licences

N/A

Awards

N/A

Conclusion and next steps

The use of MAE to manufacture SLIVER wafers for solar cells was demonstrated. SLIVERs (including spiral SLIVERs) were etched through a 650µm-thick wafer and removed. While it was shown that SLIVER etching could be achieved, the process was found to be sensitive to conditions. Future work could identify further modifications to the process which could improve the robustness of the etch. The removal of Au following SLIVER etching was also demonstrated, indicating that contamination from Au particles can be easily avoided.

Texture patterns with improved light –trapping compared to a planar SLIVER were identified and it was shown that a current improvement of 3.7% could be realised for each SLIVER wafer. Next steps would be to design and manufacture SLIVERs with these best texture patterns identified by the modelling studies.

Lessons Learnt

Lessons Learnt Report: Behaviour of thin Au films during metal assisted etching (MAE) process

Project Name: *Metal assisted chemical etching of SLIVER solar cells*

Knowledge Category:	Technical
Knowledge Type:	Technology
Technology Type:	Solar PV
State/Territory:	ACT

Key learning

The performance of the Au thin film as a catalyst for MAE is dependent on a number of factors, namely; the thickness of the film, the treatment of the film post-deposition and the etching conditions. The stability of the etch was improved through the use of thicker Au films with introduced porosity under optimised etch conditions.

Implications for future projects

The techniques developed here are the result of testing a huge range of experimental parameters. Future projects intending to use MAE for either groove etching or texturing (NB. MAE for texturing is a significant growth area in solar cell processing) will benefit greatly from the data generated here and can use it as a guide when selecting parameters for this, or other, application.

Knowledge gap

N/A

Background

Objectives or project requirements

The project objective was to develop a MAE method for the etching of SLIVER solar cells. Etching SLIVERs using this method is expected to simplify the manufacturing process as well as produce SLIVERs with optimised light trapping properties. An additional benefit is the ability to etch novel geometric shapes and improve the wafer utilisation.

Process undertaken

The steps involved in producing SLIVERs using MAE are as follows:

1. Patterning of the Si wafer
2. Depositing the Au layer
3. Heating the wafer to produce pores in the Au
4. Etching the wafer in chemical solution
5. Sample analysis and characterisation

The project involved the development and testing of a huge variety of parameters in order to determine the factors contributing to the stability and effectiveness of MAE. These parameters have included:

- Au layer thickness
- Silicon wafer pre-treatment
- Photolithography (patterning) parameters
- Au heat treatment post-deposition (temperature/time)
- Temperature of etch solution
- Composition of etch solution
- Etch conditions (light/dark, stirred/unstirred)
- Etch duration and solution replenishment over time

Samples have been analysed using optical microscopy as well as Scanning Electron Microscopy.

Supporting information

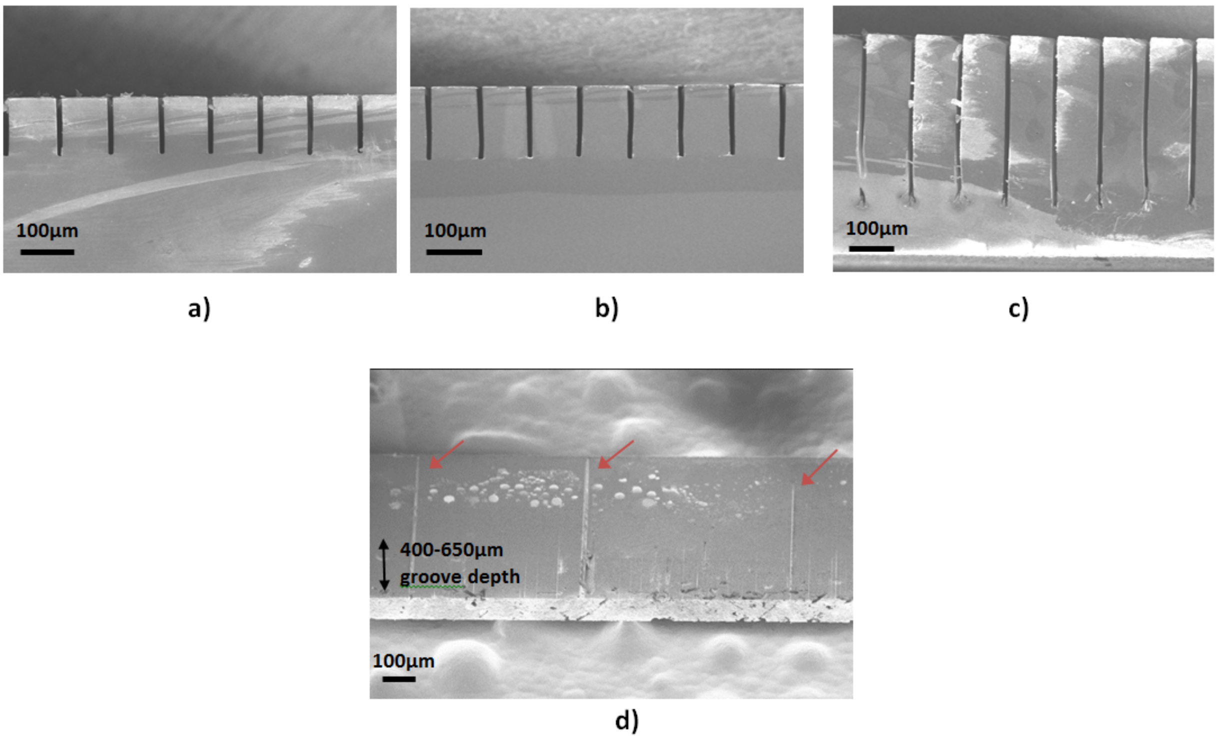

Figure 1. Grooves etched using MAE after etching for a) 1hr, b) 2hrs, c) 6hrs and d) 18hrs. The image in d) shows a SLIVER which has been removed from the wafer. The image is taken at 45° and the red arrows indicate unetched Si regions.

Lessons Learnt Report: Texture pattern for enhanced light-trapping in Sliver solar cells

Project Name: *Metal assisted chemical etching of SLIVER solar cells*

Knowledge Category:	Technical
Knowledge Type:	Technology
Technology Type:	Solar PV
State/Territory:	ACT

Key learning

Texture patterns on the front and rear surface of the SLIVER were modelled. Factors contributing to an effective texture pattern (i.e. patterns which will cause more light to be collected by the SLIVER) were ascertained, with results suggesting that current gains of 3.7% can be achieved compared to the non-textured SLIVER equivalent.

Implications for future projects

As some promising texture patterns have now been identified, future projects may move to the manufacturing of SLIVERs with these types of architectures. Additionally, these results produced some general trends in terms of the light trapping features of various surface patterns which may be applied to texturing of other thin film Si devices. Of particular importance is the effect of the bulk Si (SLIVER) thickness which needs to be kept to a minimum for there to be any overall advantage in terms of current/wafer.

Knowledge gap

N/A

Background

Objectives or project requirements

The project requirements were to develop a texture pattern that demonstrated good light trapping properties. This was to be used to guide any further development of SLIVERs produced using the MAE method. Light trapping is an important feature of SLIVER solar cells (as well as any other very thin solar cell) as it increases the amount of light that the cell can absorb, thereby increasing the current output.

Process undertaken

The investigative process involved modelling studies which were conducted using the PVLighthouse ray tracing software. Various texture patterns were modelled and included a range of feature sizes and angles on the front and the rear of the SLIVER.

Supporting information

Table 1. Summary of modelled SLIVER texture features and corresponding current output.

Feature height (µm)	SLIVER bulk width (µm)	# SLIVERs/wafer	Max current (mA/cm²)	Max current (A)/wafer
Planar	40	5950	35.07	**176.935**
5	40	5100	36.41	158.766
10	40	4462	36.46	139.095
15	40	3966	36.27*	122.989
20	40	3570	36.51	111.441
30	40	2975	36.31*	92.359
40	40	2550	36.35*	79.252
5	30	5950	36.09	183.598
10	20	5950	35.87	182.480
15	10	5950	35.23*^	179.224

Australian Government
Australian Renewable Energy Agency

ARENA

Lessons Learnt Report: Removal of Au contamination from Si after metal-assisted etch processing

Project Name: *Metal assisted chemical etching of SLIVER solar cells*

Knowledge Category:	Technical
Knowledge Type:	Technology
Technology Type:	Solar PV
State/Territory:	ACT

Key learning

The Au used for MAE was unable to be detected in SLIVERs post-processing and indicates that the removal of Au is possible using the methods employed in this project.

Implications for future projects

The complete removal of Au is highly desirable as it has the potential to greatly reduce solar cell performance if it is present during later high temperature process steps. The fact that it was successfully removed after the MAE process greatly enhances the utility of the process for solar cell applications.

Knowledge gap

N/A

Background

Objectives or project requirements

The objective was to ensure that the Si wafer was not contaminated by the presence of Au. Such contamination can potentially cause a large reduction in the ultimate solar cell efficiency.

Process undertaken

1. Decontamination- SLIVERs were treated with a solution of Aqua Regia (known to dissolve Au)
2. SLIVERs were subjected to a high temperature process in a furnace
3. Photoluminescence of the SLIVERs was compared before and after the furnace treatment. Any contamination by the Au should show as a drop in intensity of the image.
4. No reduction in intensity was detected.

Appendix

Keywords

SLIVER solar cells
Metal assisted chemical etching
Texturing
Light-trapping
Silicon

Glossary of terms and acronyms

Silicon (Si) – Material used for producing SLIVER solar cells

SLIVER solar cells – Thin, flexible solar cells made by etching out narrow Si sections (SLIVERs) from a conventional Si wafer

Groove etching – The process of producing a SLIVER, which requires numerous very narrow grooves to be etched through a Si wafer.

Metal assisted chemical etching (MAE) – A process used to etch Si which involves a metal-catalysed reaction on the Si surface.

Texturing – The process of patterning the surface of a solar cell to enhance light absorption.

Light-trapping – The mechanism by which light entering a solar cell can be "trapped" to enhance light absorption. By making the light reflect internally in the solar cell, the cell has multiple chances to absorb it.