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Collaborative project*

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<tr><td rowspan="2">Criteria and Achieved Results</td><td colspan="4">Criteria</td><td colspan="5">Achieved result</td></tr>
<tr><td colspan="4">Scaled 200 or 300 mm etch prototype with control of wafers temperature during plasma etching</td><td colspan="5">A 200mm prototype atomic layer etch tool and process</td></tr>
<tr><td>Description of the Deliverable</td><td colspan="9">We describe a 200mm plasma etch tool adapted for atomic layer etching, together with process results taken on the tool, showing saturation behavior typical of atomic layer etching (see full report starting on page 4).</td></tr>
<tr><td>Explanation of Differences between</td><td colspan="9">At the start of the project it was believed that etching at the single nanometer scale would require greater control of some of the parameters which are only loosely defined in plasma etching, notably wafer temperature. As work progressed it was realized that a cyclical atomic layer etch (ALE) process was a powerful and relevant</td></tr>
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Estimation and Realisation	technique, and work was refocused on ALE after developing an in situ wafer temperature measurement method (This was done in amendment 4 of Annex I – Description of Work)
Metrology comments	Metrology for the ALE trials used a calibrated Woollam M-2000 spectroscopic ellipsometer to measure thin films 500-1500 Å thick. Measurement repeatability of etched a-Si was ±0.7Å (1σ). Etch per cycle values were calculated from runs with 30-50 ALE cycles to ensure measurement accuracy.

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Introduction

Atomic layer etching (ALE) is a general name for a class of etching processes with the potential of removing single atomic layers. It is not uniquely a plasma etch technique: ion beam etching and even wet etching ALE methods have been developed. All share a similar approach, that the process is *cyclical*, using three or more distinct steps. The steps are illustrated in Figure 1 for the well-known example of silicon ALE using chlorine and ion bombardment.

<u>Dose</u>: the surface is loaded with reactant, preferably in a self-limiting chemisorption step. In plasma ALE this can be just gas, or radicals dissociated in a plasma.

<u>Purge</u>: excess gas phase reactants are removed

<u>Etch</u>: Energy is added to the surface, ideally causing removal of just the dose reactants and the atoms to which they are bound, so that etching stops once the reactants are gone

<u>Pump</u>: Reaction products are removed. In plasma ALE, this step can often be omitted, unless there are unwanted reactions possible between reaction products and the next dose step.

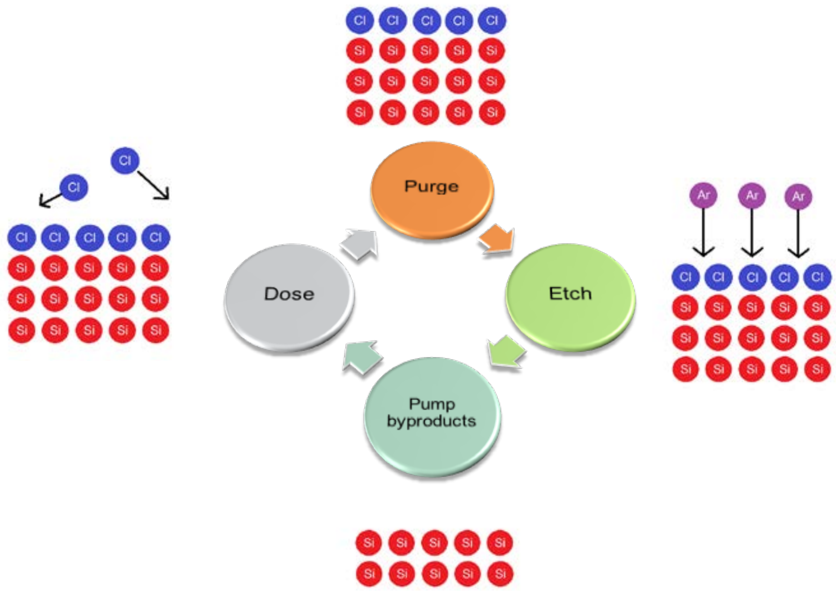

Figure 1 Schematic of silicon atomic layer etch cycle

Those interested in learning more about the technique are referred to early literature[1,2] and examples of recent work[3,4]. The atomic layer deposition conference series has included a significant ALE workshop since 2014; the most recent conference was in Dublin in 2016 (http://ald2016.com/).

Etch tool hardware

The basis of the atomic layer etch tool is a conventional plasma etcher (Oxford Instruments PlasmaPro 100), with a 300 mm induction coupled plasma source (3 kW, 2 MHz) and an RF biased table (600W, 13.56 MHz). The table temperature is controlled by recirculated fluid, while heat transfer to the wafer is enhanced by mechanical clamping and helium gas injection at controlled pressure (around 10 mbar) behind the wafer. Gases are supplied via mass flow controllers (MFC), and the tool is pumped by a 1600 litre/second turbomolecular pump backed by a 100 m^3/hour dry pump. The process pressure range is typically 5 – 30 mTorr, measured by a capacitance manometer and controlled by an automatic throttle valve. Sample entry is via a load lock in this work; the same process chamber can be clustered with others and loaded from a vacuum cassette.

Figure 2 PlasmaPro 100 etch tool with 200 mm wafer load lock.

The special requirements of atomic layer etch include:

- Small, repeatable gas doses
- Ion bombardment energy controlled in the range 20 – 50 eV
- A cyclical recipe with repeatable timing

We consider these individually. The hardware is subject to a patent application.[5]

Gas dose

In earlier work, it was found that the minimum gas pulse time from a conventional gas box was around 1 second, dominated by the MFC response time. The transit time from the gas box shifted the time of the gas pulse by a fraction of a second. Tests with a close-coupled gas box used for cyclical deep silicon etch were also unsatisfactory: these are optimized for rapid injection of high flows. Further, the flows are not turned off; instead flow is cycled between low and high values, which is not suitable for ALE. (If the gas is turned off completely, then the dose when turning on depends on the leak-tightness of the MFC and the off time, leading to instantaneously high and irreproducible gas doses.)

Taking learning from atomic layer deposition, a continuous flow of the chemical gases were used, with fast acting valves close to the chamber, while other gases such as argon were not pulsed but were controlled from the gas box as normal. Chemical gases either enter the chamber or are diverted to the foreline vacuum.

With this method, a minimum gas dose time of 10msec can be selected, with an incremental resolution of 1 msec. Typical recipes use 20 – 40 msec doses. The response of the system is shown in the graphs below. In the first test, a succession of CHF_3 gas pulses of increasing duration between 5 and 7000 msec were applied, and the optical emission at 516 nm was measured. Pulses below 10 msec gave no measurable response, but longer pulses gave distinct responses. Above 500 msec, the pulses start to take increased time to decay, and above 4 seconds the decay to floor is not complete before the next pulse begins, 40 seconds later.

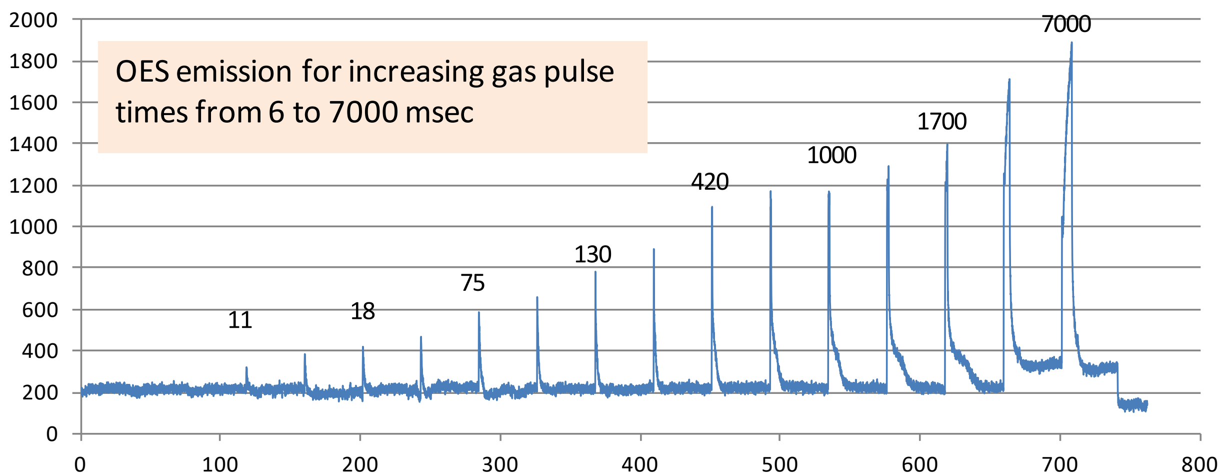

Figure 3 Optical emission from plasma with gas pulses increasing from 6 msec to 7 seconds long, spaced 40 seconds apart

The optical emission spectroscopy (OES) peak intensities, and an integrated peak area (emission intensity x time) are plotted below as a function of gas pulse length. The maximum emission goes through three distinct regions, with longer pulses tending to a saturated steady state condition. The integrated peak area over each pulse is approximately linear with pulse length, as required for a controlled dose.

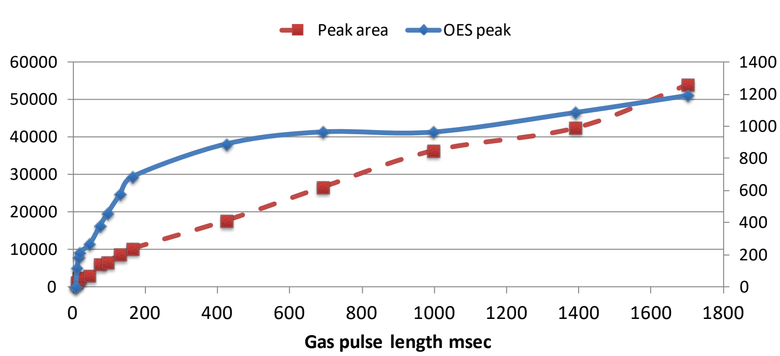

Figure 4 Optical emission spectroscopy (OES) maximum (blue) and peak area (dashed red line) v. gas pulse length

Ion bombardment

A plasma excited at 13.56 MHz is a rectifier, because:

- Electron number density in the plasma is almost identical with positive ion density (assuming negative ions are not present);
- Electron velocities are far higher than ion velocities at the plasma boundary (so electron fluxes are higher than ion fluxes)

This generates a negative DC offset at all surfaces in contact with the plasma, which equalizes the positive ion and electron fluxes to the surface, unless a DC current is drawn at the surface. The electrons respond to the instantaneous electric field, while ions tend to respond to average fields due to inertia. The ion bombardment energy at the surface of an RF-driven electrode has a spread, depending on the RF frequency and the plasma potential, but the peak energy scales linearly with the DC offset. Effectively, the RF power applied to the wafer table controls the ion bombardment energy. Conventionally the dc offset is called ‘DC bias’ and is quoted as a positive value. Note that this is plasma effect, not a bias applied by an external voltage.

The variation of DC bias with RF power to the table is shown below, with a detailed view of the variation at low RF power.

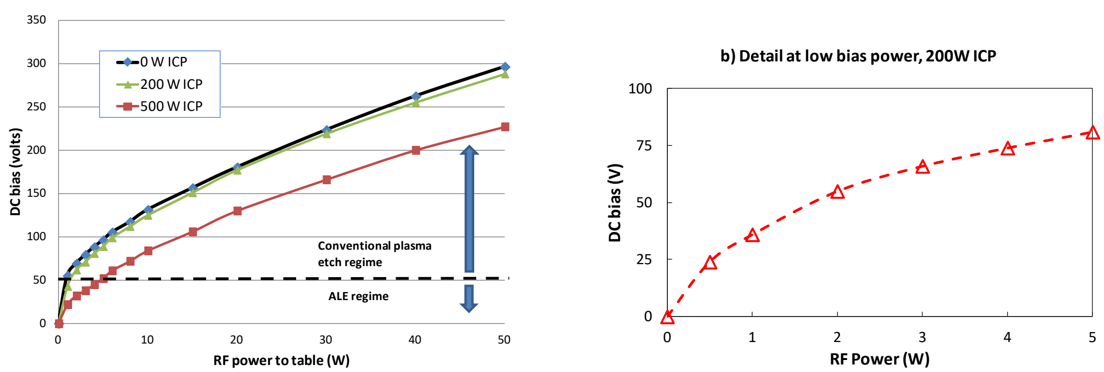

Figure 5 a) DC bias v RF power to table. b) Detail for low RF bias power at ICP 200 W

Atomic layer etching operates in a narrow range of ion bombardment energy, typically 20 – 40 eV, sufficient to promote desorption of chemically bound species, but below the sputter threshold for the underlying material. Control of the bias power to a fraction of a watt is not normally possible with a generator of 300 W or more, typically used for plasma etching. An RF bias kit has been designed and tested which can deliver power reproducibly in both a low power and high power range, so the process chamber can perform both standard etching and atomic layer etching.

Cyclical recipes

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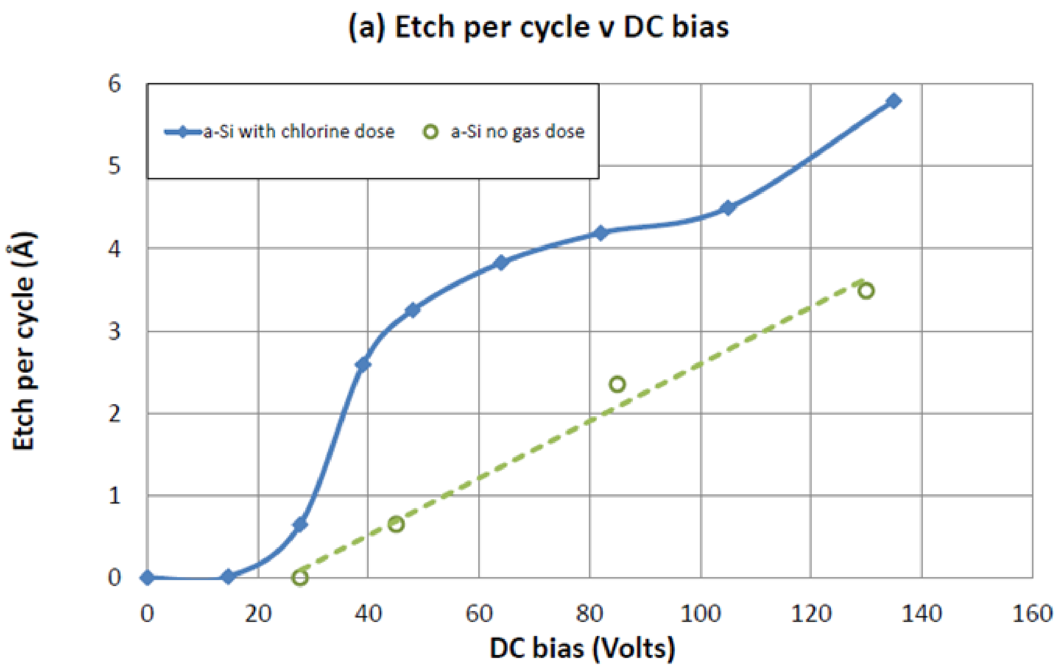
Industrial plasma etchers have used embedded programmable logic controllers (PLCs) for robust, fast control since the 1990's. A front end PC manages the user interface and communicates with the PLC. PLC cycle times have reduced in the last twenty years, so that individual devices can be read or set with millisecond resolution. It still requires care to write the PLC code appropriately, so that the most critical devices are timed appropriately.

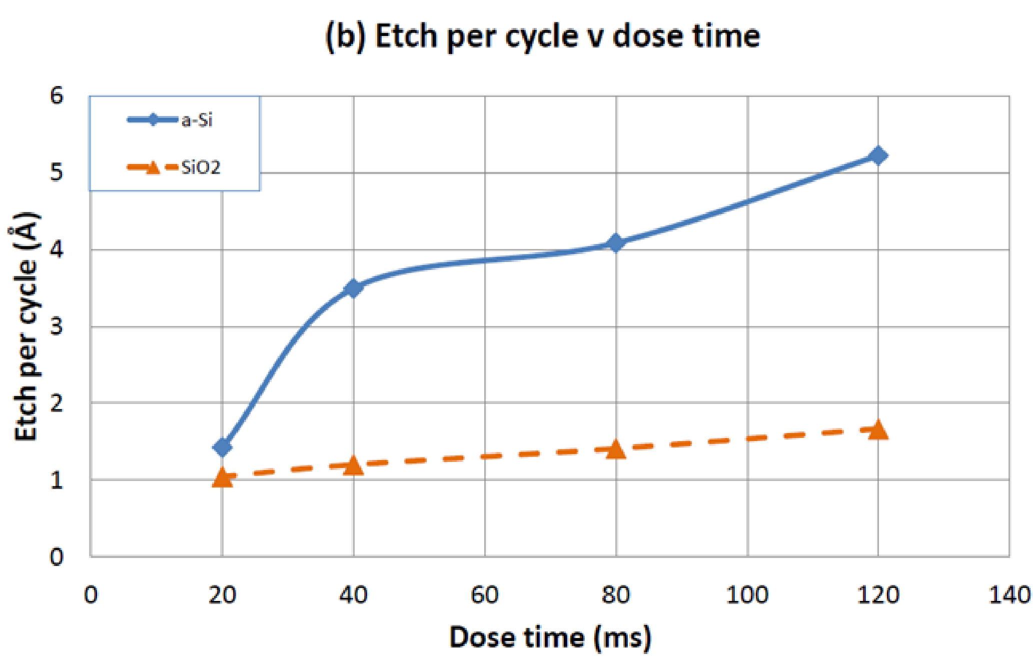
The internal system architecture formerly operated a recipe step-by-step, downloading the next step when the previous step had finished. This is appropriate for a recipe of a few steps, but introduces cumulative delays and timing jitter in fast cyclical recipes. It is necessary to download the entire recipe sequence to the PLC at the start, and manage execution within the PLC for atomic layer etch processes. It is not enough just to use a fast PLC.

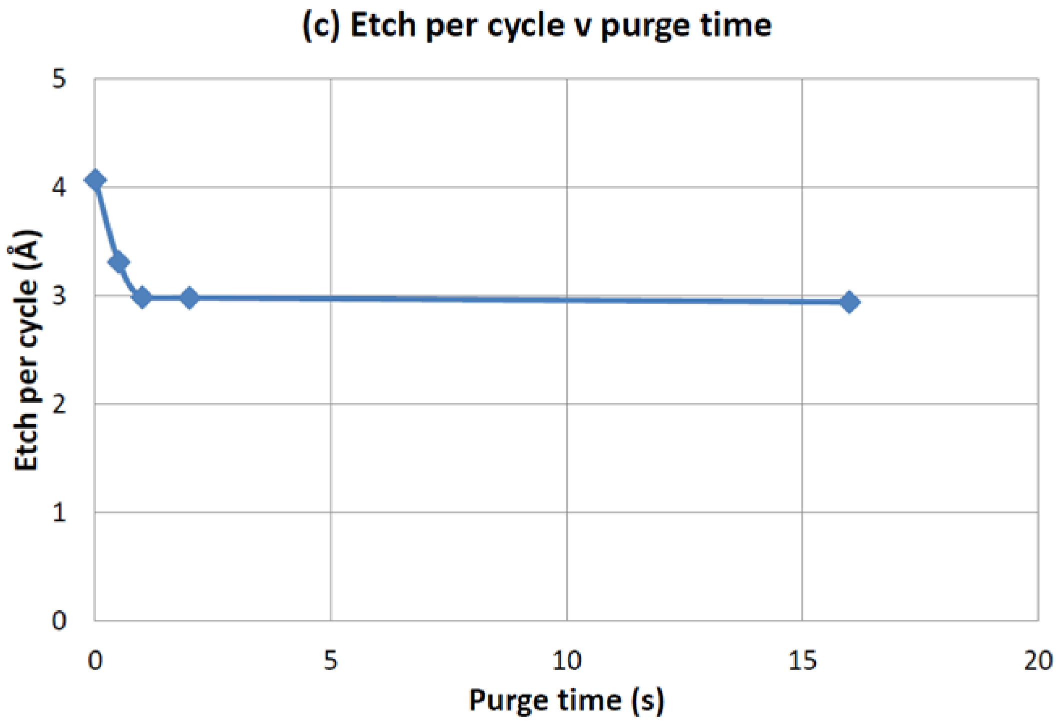
Process results

Silicon ALE

One of the results expected for a self-limiting process is that the etch rate is constant as one of the input parameters is varied, for example, the amount of chemical gas dose or the duration of the etching step. Extended plateau regions are not typically observed, because ideal behaviour is in competition with other processes. For example, if the chemical gas dose is extended, then the purge step must also be lengthened to prevent chemical gases being present during the ion bombardment step, otherwise fresh reactants are supplied to the surface during bombardment and the process reverts to basic plasma etching. RF bias power is similarly critical, because there is little separation in energy between beginning to remove chemisorbed species and starting to sputter atoms by non-chemical momentum transfer.


(a) Etch per cycle v DC bias
a-Si with chlorine dose
a-Si no gas dose
Etch per cycle (Å)
DC bias (Volts)
0
1
2
3
4
5
6
0
20
40
60
80
100
120
140
160


(b) Etch per cycle v dose time
a-Si
SiO2
Etch per cycle (Å)
Dose time (ms)
0
1
2
3
4
5
6
0
20
40
60
80
100
120
140



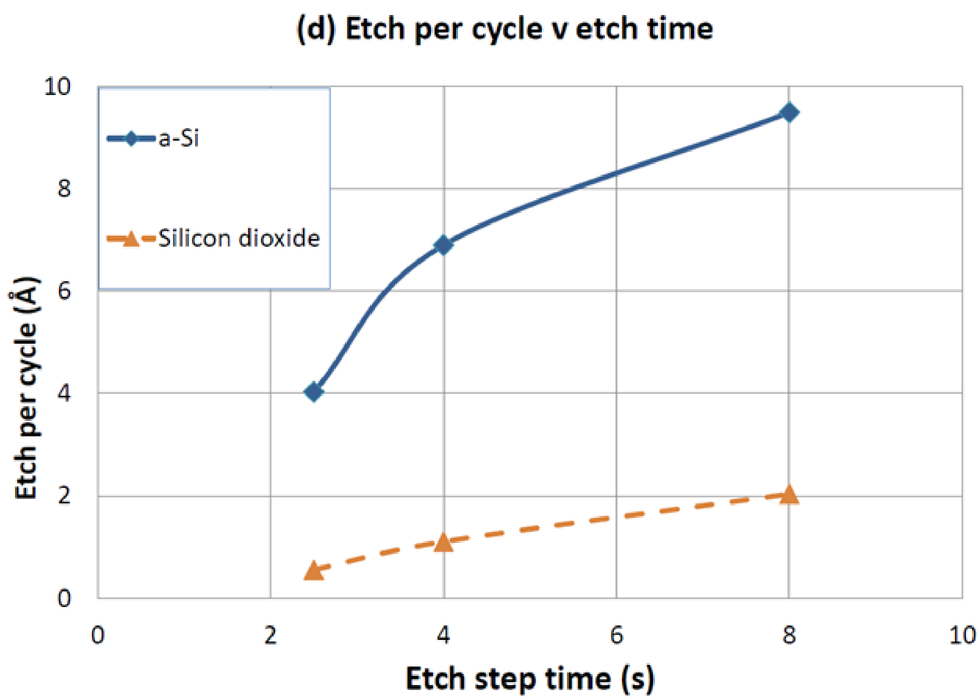


Figure 6 Saturation curves for silicon atomic layer etching

Figure 6a gives the etch rate of amorphous silicon and and PECVD silicon dioxide in a chlorine/argon cyclical recipe for different values of DC bias. SiO_2 is not significantly etched by chlorine, but the onset and increase in sputter etching is seen. Silicon etches faster, and with a clear inflection region between 40 – 100 eV, above which the rate rises. Another series is shown in Figure 6b, where the dose time is varied. Figure 5c shows that a purge time of just a few seconds is sufficient after the gas dose, provided a short dose is used (below 40 msec). The etch per cycle shows an inflection, but no plateau, probably because the ion bombardment energy for these tests was higher than ideal.

Experimental details are in a paper recently published in the Journal of Vacuum Science and Technology (A Goodyear, M Cooke 2017)[6]

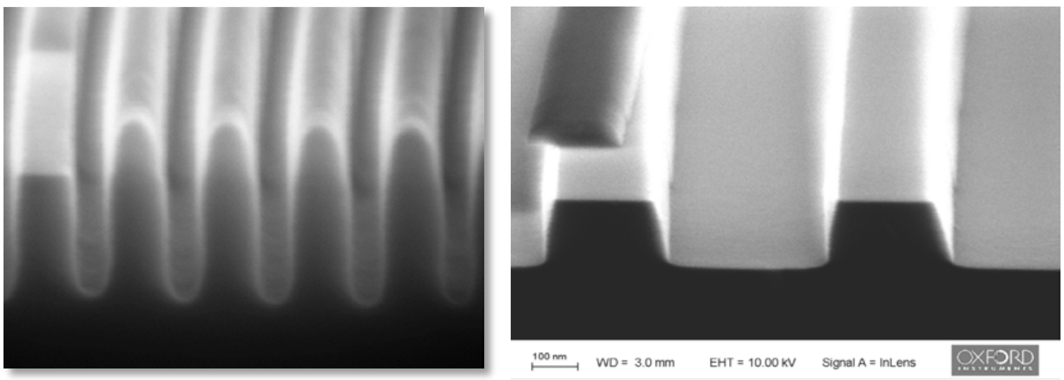


Figure 7 Silicon etched by an ALE process, mask still in place

The optimized ALE process was used to etch 110 nm deep, 25 nm wide, trenches in crystalline silicon using an HSQ mask written by electron beam lithography. The anisotropic etch is shown in Figure 7. The etched surface is smooth (by SEM view) and at the aspect ratios tested (up to 4:1), the aspect ratio dependent etch rate effect is low.

MoS_2 ALE

Molybdenum sulphide films grown by chemical vapour deposition were etched in a chlorine/ argon ALE cycle similar to that used for silicon etching, and characterized ex situ by Raman spectroscopy. The separation of peaks around 382 and 406 cm^{-1} indicate the number of MoS_2 layers present. If the material is disordered, a peak appears at 227 cm^{-1}. The peak separations change as more etch cycles are applied, indicating that etching is taking place. It is particularly interesting that the 'disorder' signal does not appear, suggesting that the cyclical process may be useful in device fabrication using 2D materials.

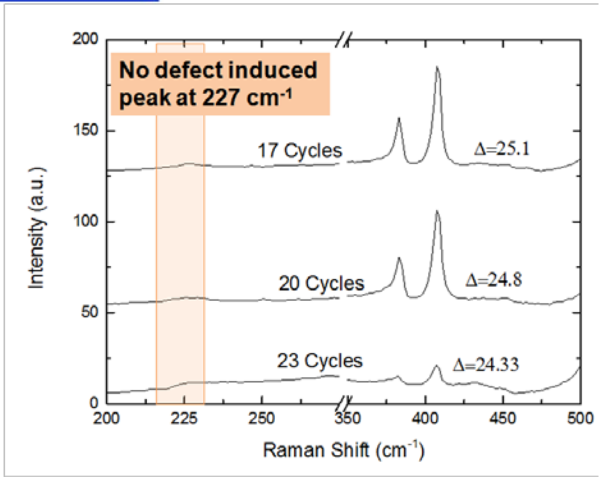


Figure 8 Moybdenum sulphide etched by ALE

Summary

A process module has been developed for atomic layer etching, using controlled doses of a gaseous chemical and low energy ion bombardment. A process for atomic layer etching of silicon has been characterized, and first results obtained for a cyclical etch process for molybdenum disulphide.

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[4] Samantha Tan, Wenbing Yang, Keren J. Kanarik, Thorsten Lill, Vahid Vahedi, Jeff Marks, and Richard A. Gottscho ECS J. Solid State Sci. Technol. 2015 volume 4, issue 6, N5010-N5012
[5] A. Goodyear and M. Cooke European patent application EP16187143 (3 September 2015)
[6] A. Goodyear and M Cooke J. Vac. Sci. Technol. A 35, 01A105 (2017); doi: 10.1116/1.4972393