

# Real-Time Monitoring of Spontaneous and Plasma Enhanced Si Etching Processes with the pgaTOF

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Optical spectroscopy and mass spectrometry are the primary technologies used for etch process characterization and monitoring. Optical techniques are desirable in production settings because of their non-invasive nature, but they are applicable only in specific cases and cannot address all chemistries and materials. By contrast, mass spectrometry is a powerful technique for analysis of any process gas. Integrating mass spectrometers requires careful consideration of differences in process flow, pressure and reaction time scales. These constraints have previously been addressed using quadrupole mass spectrometers (residual gas analyzers, RGAs). However, as the semiconductor industry incorporates more materials in highly complex stacks for design of the next-generation chips, the limited mass range and low mass resolution and sensitivity of RGAs create a situation where they are no longer able to meet all the challenges of integration.

## The TOFWERK Process Gas Analyzer

TOFWERK's pgaTOF is an electron ionization time-of-flight mass spectrometer that was developed specifically to overcome the limitations of RGAs. The pgaTOF provides simultaneous detection of all ionized species with isotopic resolution, greater than  $10^5$  dynamic range and a mass spectral acquisition rates up to 1000 Hz. All process gas and etch products are monitored to guide process control action and to inform analytics and process intelligence. Immediate modifications of process conditions include optimizing flow rates and ratios, monitoring substrate temperature, or detection of process excursion from optimal conditions or malfunctions.

## Spontaneous and Plasma Enhanced Etching of Silicon

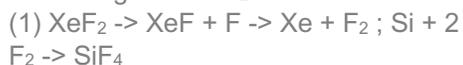
In this proof-of-concept etch experiment with the pgaTOF, two well-studied, semiconductor-relevant chemistries were investigated - spontaneous Si etching in  $\text{XeF}_2$  and plasma etching of Si in a  $\text{CF}_4/\text{O}_2$  chemistry.

The pgaTOF was connected to the process reactor through a ~1 meter bellow. In the spontaneous etch case, the pgaTOF was connected directly to the reactor chamber. For the plasma etch system, the pgaTOF was connected at the rough pump level. Process pressures were varied from approximately 3-400 mTorr ( $\approx$  mbar), with sample temperature ranging from 20 C to just over 200 C.

The expected etch reactions for both XeF<sub>2</sub> and CF<sub>4</sub>/O<sub>2</sub> conditions are shown below. Note that in a pure CF<sub>4</sub> plasma, non-volatile carbon compounds accumulate on the sample surface, hindering surface chemistry and resulting in lower etch rates and rough surfaces. Adding O<sub>2</sub> to the etch gas results in the reaction of these non-volatile compounds and formation of CO<sub>2</sub>, greatly increasing the etch rate.

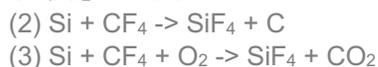
### Spontaneous Etching of Si in XeF<sub>2</sub>

Si Etching with XeF<sub>2</sub>



### Plasma Etching in a CF<sub>4</sub> and CF<sub>4</sub>/O<sub>2</sub> chemistry

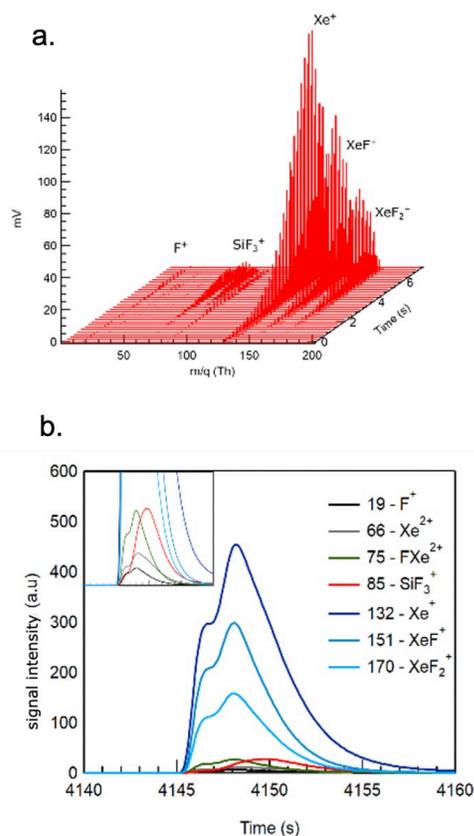
Si etch reactions are shown below for a pure CF<sub>4</sub> plasma (2) and (3) for a CF<sub>4</sub>/O<sub>2</sub> mixture



### Experimental Results

Spontaneous Etch of Si with XeF<sub>2</sub>

Si samples (3 cm<sup>2</sup>) were inserted in an atomic layer deposition (ALD) reactor fitted with a XeF<sub>2</sub> source with variable pulsing capability using Ar as a carrier gas.



**Figure 1.** Spontaneous etching of silicon with XeF<sub>2</sub>. Figures 1a (top) and 1b (bottom) show the time evolution of the most abundant species as the etch gas is introduced in a pulsed mode (100ms and 0.5mbar in an Ar carrier gas).

Figure 1 shows all relevant species and their time variation as a XeF<sub>2</sub> pulse is introduced in the reactor. Figure 2 displays the same data with varied pulse width. Detailed analysis of data in Figure 2 demonstrates that real-time optimization of the etch gas flux and resulting by-products is possible. Similarly, as in the ALD case, and more importantly in an atomic layer etching process, this points out the ability to determine the optimum time needed to purge out the by-products prior to initiating the next process

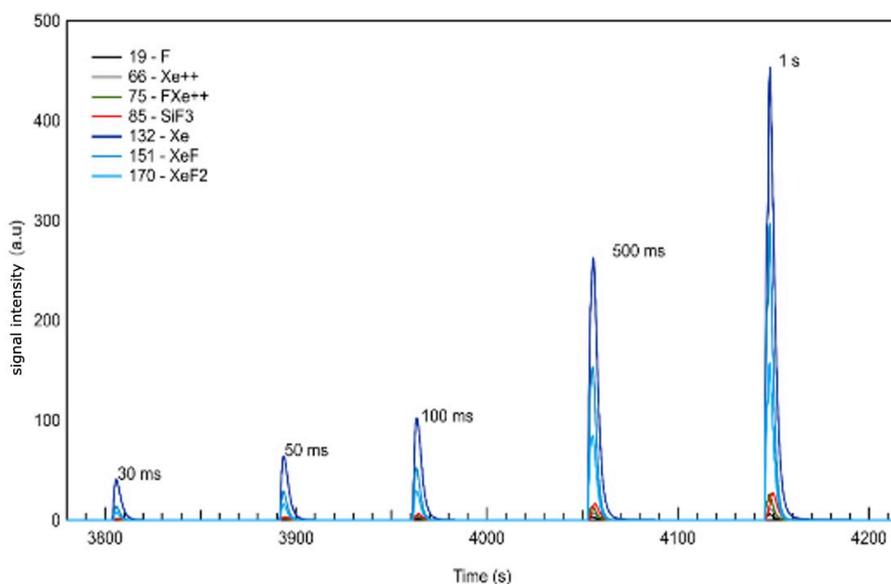
cycle. Also, during process development and optimization such a capability permits detection of a transition from an etch-rate-limited mode to loading-limited conditions. An important observation is that despite the very small sample size, large signal counts are measured for all species. Based on previous results and published literature for this etch chemistry, etch rates significantly smaller than one monolayer per second are expected for these process conditions. Finally, with the time-of-flight technology of the pgaTOF all compounds - whether known in advance or not - are recorded and stored for off-line analysis, understanding and forensics.

### Reactive Ion Etching of Si in a $\text{CF}_4/\text{O}_2$ Chemistry

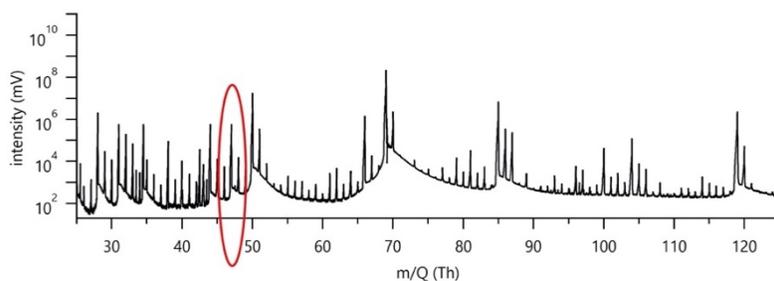
Experiments were conducted in both a downstream microwave plasma etcher and a standard reactive ion etch chamber (RIE). In both cases, only cm-sized Si substrates were utilized. Runs using both pure  $\text{CF}_4$  and  $\text{CF}_4/\text{O}_2$  etch mixtures were performed at varying pressures and substrate temperatures.

Figure 3 displays typical low-mass data for a pure  $\text{CF}_4$  RIE etch run. Despite the simple etch chemistry and the most basic substrate, the collected spectrum is dense with peaks.

Figure 4 shows the time dependence of relevant species in the mass spectrum as the plasma is turned on and off and the  $\text{O}_2$  content in the  $\text{CF}_4$  plasma is increased.



**Figure 2.** Spontaneous etching of silicon with  $\text{XeF}_2$  showing the signal time variation of the most abundant species as the etch gas is introduced using pulses of different duration (0.5mbar in an Ar carrier gas).



**Figure 3.** Typical spectrum during a Si etch run in a pure CF<sub>4</sub> plasma (400 W, 100 sccm CF<sub>4</sub>)

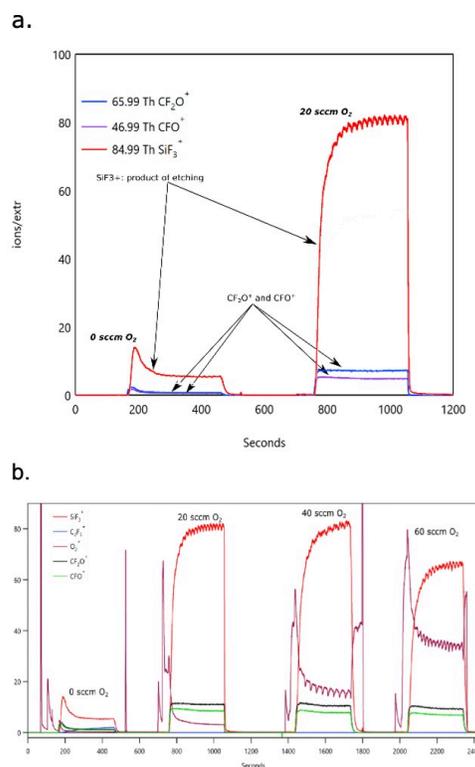
As expected, the abundance of etch products significantly increases with O<sub>2</sub> content but ultimately reaches a maximum at ~ 40 sccm (figure 3b) and decreases beyond that value due to reactive species dilution. Of interest, as a result of small variations in O<sub>2</sub> flow rates, we observe measurable oscillations in the etch product signal which become significant as we go beyond the optimum O<sub>2</sub> concentration (max etch rate) and move into the reactive species deficient regime. Such behavior is probably not critical in thick layer etching but would need to be corrected for when processing nanostructured devices.

### pgaTOF Records All Compounds and Isotopic Distributions with High Mass Accuracy

As demonstrated in this proof-of-principle example, even the simplest etch chemistry (i.e., Si in a CF<sub>4</sub> plasma) yields complex mass spectra where assignment of the observed peaks is not always easy or possible.

To that end, we would like to illustrate the challenge to identifying the peak at 47 Th, as highlighted in Figure 3 within the red circle, to a specific etch gas or product specie.

For the pure CF<sub>4</sub> plasma chemistry and substrate at play, the only possible species should have combination of the input etch gas and substrate atomic constituents, C, F, and Si.



**Figure 4.** Time evolution of plasma and etch product species during a CF<sub>4</sub> RIE process showing the effect of O<sub>2</sub> addition on the etch rate. a. (top) Power: 400 W, 100 sccm CF<sub>4</sub>, variable flow of O<sub>2</sub> (0, 20 sccm), b. (bottom) Power: 400 W, 100 sccm CF<sub>4</sub>, variable flow of O<sub>2</sub> (0, 20, 40 and 60 sccm).

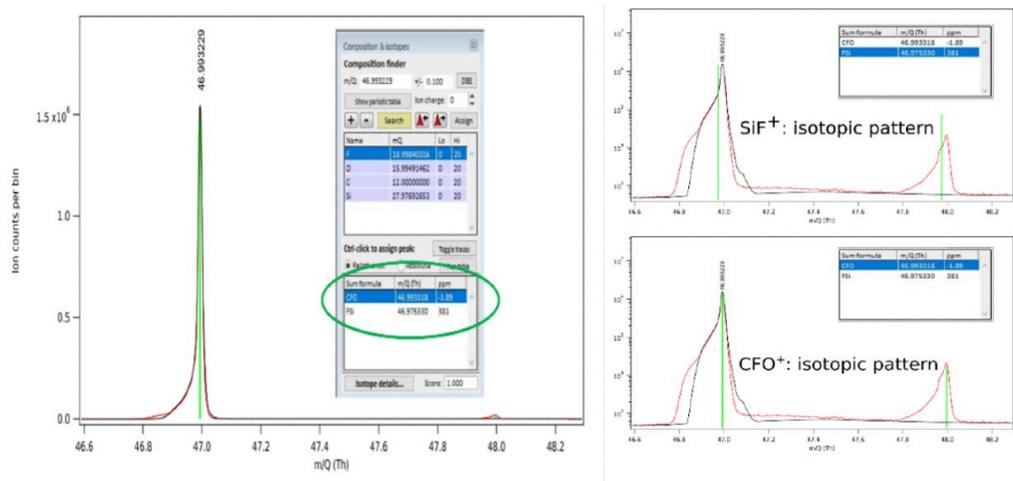


Figure 5. Identification of peak at 47 Th in the spectrum acquired during Si etch in a pure  $CF_4$  plasma using the instrument's high mass accuracy (left panel) and measured isotopic distribution peaks with expected position for the two possible species (right panel)

Using the composition finder function of the pgaTOF's software gives the etch product  $SiF^+$ , at 46.974 Th (383 ppm mass deviation from measured peak) as a possible assignment. Full mass spectral acquisition, however, allows detection of a small but measurable  $O_2$  signal which expands the possible species to oxygen containing compounds. The composition finder gives us  $CFO^+$  at 46.992 Th (0.2 ppm mass deviation from measure peak) as another match.

Assigning the correct specie to the peak at 47 Th in this case is paramount to better understanding of the etch chemistry but more importantly key to determining whether process integrity is acceptable or not;  $SiF^+$  being an expected etch product but  $CFO^+$  an unexpected impurity related specie. Figure 5.a summarizes these results. To further improve our mass assignment, we look at the isotopic

distribution for the two possible species and their match to the experimental pattern. Fig 5.b shows the isotopic distribution for both species and it is evident that only  $CFO^+$  presents a good visual match. Armed with these two observations, the peak at ~ 47 Th is unambiguously assigned to  $CFO^+$  which can point to a possible leak ( $O_2$  flow meter or external) or other contamination sources.

## Conclusion

A mobile pgaTOF instrument connected to an etch reactor in a minimally invasive fashion has been shown to provide important process insights even for the simplest etch chemistry ( $CF_4/O_2$ ) and the most basic substrate (Si). Demonstration of real-time monitoring of all volatile compounds with high mass accuracy and sensitivity and sub-second detection of process changes was shown. The pgaTOF's ability to

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measure masses with very high accuracy and resolution is found to be critical in unambiguous species assignment. Intrinsic measurements of all species allows for on-line reactor health assessment and off-line data analysis for process optimization and failure analysis.

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