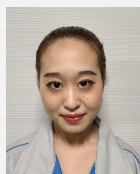


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Mass spectrometric analysis of SiN etching processes in CHF₃/O₂ plasma



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A quadrupole mass spectrometer (QMS) was applied to observe the changes in gas species during the SiN etching in CHF₃/O₂ plasma. Under the condition without O₂, the main detected ions are CF₃⁺ and CHF₂⁺ decomposed from CHF₃ gas. The fluorocarbon ions with molecular weights larger than CHF₃ were also observed, indicating that polymers are formed in the gas phase, which prevent the SiN etching. On the other hand, under the condition with adding O₂, CF₃⁺, CHF₂⁺ and CF⁺ signal intensities decreased by more than the decrease in the CHF₃ flow rate, whereas CO₂⁺ and CO⁺ signals increased. Adding O₂ had an effect on an increase in the SiN etching rate. Accordingly, SiF₃⁺, SiF₂⁺, SiF⁺, the SiN etching byproducts, were detected.

Introduction

In recent years, there has been a noticeable increase in collecting and analyzing large amounts of data from process equipment. The utilization of this data to detect abnormalities at an early stage and to improve quality of the processes has been enabled by the rapid advancement of data storage and analysis capabilities. Thanks to the evolution of semiconductor hardware and software, vast amounts of data can be stored and processed. Access to data and analysis that affects the quality of processed wafers is important for the smart fab concept [1].

The current main application of the quadrupole mass spectrometer (QMS) in vacuum processes is residual gases monitoring, we refer to this data as "Condition monitoring". Figure 1 shows the trend of residual gases during vacuuming after chamber maintenance. H₂O is readily absorbed to the chamber inner wall. By applying a baking process during the initial pump down of the process chamber, residual H₂O partial pressure can be reduced by an order of magnitude. Users can set a threshold pressure at which the production process can be started, or multiple gas data can be used to develop an algorithm to determine it.

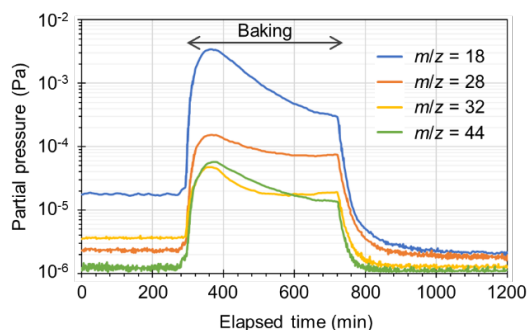


Figure 1. Typical *m/z* peak trends from series of mass spectra during vacuuming.

Another QMS application is "Process monitoring" that enables the real-time observation of changes in gas species in a chamber during wafer processing. There are many process parameters, e.g. gas flow rates, that determine the quality of processes, most of which are controlled precisely through process recipes. When it comes to direct monitoring the inside of a chamber, only optical emission spectroscopy (OES) is used for plasma processes in mass production. Although OES has been an essential technology for plasma diagnostic, the QMS has advantages, such as monitoring during non-emission

state in the myriad of complex processes required for advanced semiconductor manufacturing.

This article reports the results of the application of the in-situ QMS to plasma process monitoring. The QMS is attached to a dielectric etching chamber to observe changes in gas species during SiN etching. The effectiveness of process monitoring with the QMS is examined through a series of experiments.

QMS principle

A QMS consists of the three parts: an ion source, an analyzer and a detector as shown in Figure 2. The measurement proceeds as follows [2]:

1. Thermal electrons emitted from the filament collide with process gases, resulting in ionized gas species.
2. The positive ions are extracted by the ion lens and introduced into the quadrupole analyzer, where DC and AC voltages are applied to the rods. By combining the voltages conditions, only ions with a specific mass-to-charge ratio, expressed as m/z, can pass through the rods. This forms the Mass Filtering functionality of the QMS.
3. The ions of a selected mass-to-charge ratio pass through the analyzer to collide with the Faraday cup and generate small amount of ion current. Faraday cup detectors have good linearity between current and the number of detected ions. By setting the appropriate conversion factor, the ion current can be converted to the partial pressure of each ion.

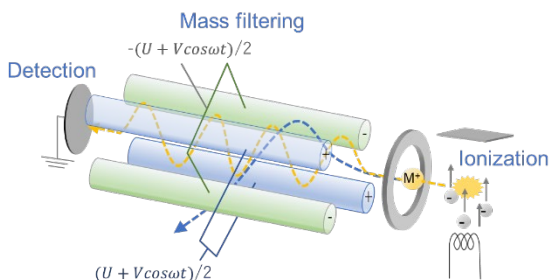


Figure 2. Schematic diagram of a QMS.

Experiment

A schematic diagram of the experimental setup is shown in Figure 3. A QMS (HORIBA MICROPOLE system) with a differential pumping system is attached to the reactive ion etch chamber for plasma measurements. The chamber pressure and the pressure at the QMS during the etching process are maintained to 5 Pa and 0.01 Pa, respectively. The electron impact energy in the QMS is set to 70 eV. The CHF₃ and O₂ flow rates are controlled by the mass flow controllers in such a way that the total flow rate is held constant at 30 SCCM. The RF power at 13.56 MHz is set to 150 W. Plasma enhanced chemical vapor deposition-grown SiN layers on Si substrate were prepared for this experiment. Etching rates were confirmed by the ellipsometry (HORIBA AutoSE).

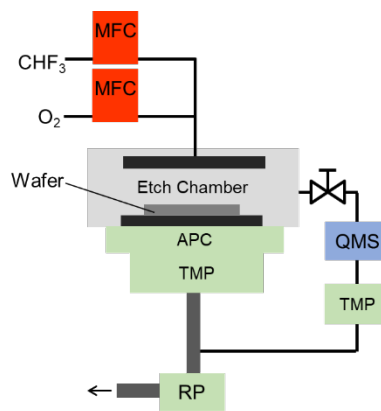


Figure 3. Schematic view of the RIE system with the QMS.

Results

1. SiN etching rate

Shown in Figure 4 are the etching rates for different CHF₃/O₂ flow rates. No significant etching was observed under the condition without O₂. The etching rate drastically increases when O₂ is added and shows a maximum at the CHF₃/O₂ = 12/18 SCCM and then gradually decreases with decreasing CHF₃/O₂ ratios. Notice that etching of about 40 nm/min occurs under the condition of CHF₃/O₂ = 0/30 SCCM, indicating that physical etching by oxygen ions is dominant in this condition. On the contrary, etching with CHF₃/O₂ = 30/0 SCCM does not proceed, which is considered to be due to the fluorocarbon polymer deposition from the CHF₃ plasma [3]. Compared with CF₄, CHF₃ gas includes hydrogen, which is more easily dissociated than fluorine, resulting in polymer formation on the samples. Moreover, dissociated fluorine from CHF₃ is scavenged by hydrogen, which also promotes polymer deposition. Adding O₂ works in reverse to hydrogen, decreasing the polymer thickness by reacting with carbon, leading to CO and CO₂ generation, which are readily pumped away from the chamber. As the polymer thickness decreases, accelerated ions collide with the sample surface and provide enough energy at the polymer/SiN interface for promoting chemical etching.

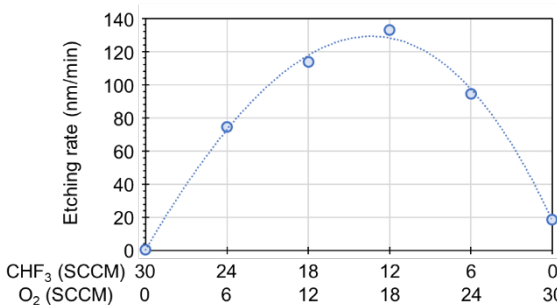


Figure 4. CHF₃ and O₂ flow rate dependence of SiN etching rate, for the RF power was 150W and the chamber pressure was 5 Pa.

2. In-situ mass spectrometric monitoring

Figure 5 (a) and (b) shows the mass spectra during the SiN etching for the CHF₃/O₂ flow rates of 30/0 SCCM and 12/18 SCCM, respectively. In the lowest etching condition of CHF₃/O₂ = 30/0 SCCM (Figure 5 (a)), the main detected ions are CF₃⁺ and CHF₂⁺. Since CHF₃ gas decomposes into CF₃⁺ and CHF₂⁺ as the first step by the electron impact in the QMS, namely fragmentation, these ions were observed under both plasma-on and plasma-off conditions. There are oxygen-containing ion peaks such as CO, even though no oxygen gas is introduced. This is believed to be due to the residual oxygen-related gases and the exposure of quartz parts to the etching gas. It is notable that C₂F₃⁺ and C₃F₃⁺ were detected for the only plasma-on condition, indicating that some fluorocarbon radicals polymerize in the gas phase.

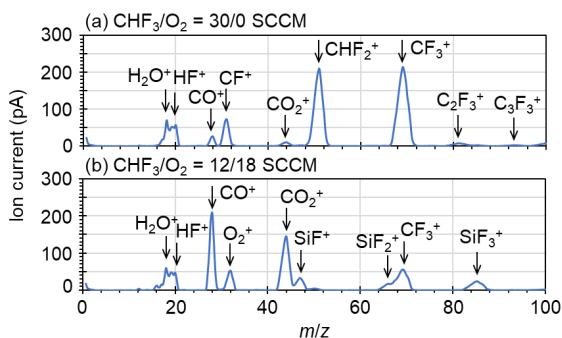


Figure 5. Mass spectra under the flow conditions: (a) CHF₃/O₂ = 30/0 SCCM and (b) CHF₃/O₂ = 12/18 SCCM.

In the highest etching condition of CHF₃/O₂ = 12/18 SCCM (Figure 5 (b)), CF₃⁺, CHF₂⁺ and CF⁺ signal intensities decrease by more than the decrease in CHF₃ flow rate, whereas CO₂⁺ and CO⁺ signals increase. This result supports the SiN etching mechanism by CHF₃/O₂ plasma that oxygen radicals and ions decrease fluorocarbon polymer which works as a barrier to SiN etching, allowing the reaction between SiN and fluorine [4]. Silicon-containing ions, SiF₃⁺, SiF₂⁺ and SiF⁺, were

also detected as etching by-products. The behavior of these peaks with respect to the CHF₃/O₂ ratio is in good agreement with that of the SiN etching rate. There should be a correlation between the SiN etching rate and the amount of SiF_x byproducts. The mass spectrum detected in this experiment, however, came from the gases in the piping of the differential pumping system attached to the side of the chamber. The gas composition in the chamber does not necessarily match the gas composition in the differential pumping system piping. When a QMS with differential pumping system is used for quantitative evaluation, it is necessary to pay attention to the mounting, the amount of suction, total gas flow and so on.

Conclusion

An example of process monitoring by using the QMS during SiN etching is presented. In order for the QMS to be used as a robust process monitoring tool, the challenges that increasing lifetime of the filament and expanding pressure operating range are crucial. Nonetheless, adding oxygen to CHF₃ plasma changes SiN etching rates, the mechanism of which can be explained by mass spectrum changes in this experiment. One of the strong points of a QMS for plasma process monitoring is that relatively heavy gas species such as C₂F₃⁺ and SiF₃⁺, the molecular species difficult to detect with OE S, can be identified. We expect that several process monitors including a QMS will be used in combination, taking advantage of their respective characteristics in the future.

Reference

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