

# SiO<sub>2</sub> and SiN etching by Low Global Warming Potential Gas

Since the 1997 Kyoto Protocol (COP3), many people have been attempting to stop global warming. Scientists who conduct research using the dry etching and deposition processes are no- exception to the requirement to reduce greenhouse gas (GHG) exhausts . Since 1995 (before COP3), we at Samco have been researching systems that capture and disintegrate perfluorocarbon compounds (PFCs).

This article introduces Samco’ s recent research on dry etching with carbonyl difluoride (COF<sub>2</sub>), which has lower global warming potential (GWP) than tetrafluoromethane (CF<sub>4</sub>) and trifluoromethane (CHF<sub>3</sub>).

## Introduction

CF<sub>4</sub> and CH<sub>3</sub> gases are commonly used in dry etching of silicon dioxide (SiO<sub>2</sub>) and silicon nitride (SiN) films. However, use of these gases is to be reduced in accordance with COP3 guidelines, because their GWP is high, as shown in Table 1. Samco has studied the feasibility of COF<sub>2</sub> as an alternative to CF<sub>4</sub> and CH<sub>3</sub>.

COF<sub>2</sub> was developed in New Energy and Industrial Technology Development Organization (NEDO) project as an alternative to PFC. Some researchers reported that COF<sub>2</sub> was used to clean the chambers after Chemical Vapor Deposition (CVD), but COF<sub>2</sub>’ s use in etching has not been reported yet. We discovered that COF<sub>2</sub> can etch SiO<sub>2</sub> film, as it can function as a cleaning gas following CVD. Additionally, Samco has determined that COF<sub>2</sub> could be broken down into carbon monoxide (CO) and Flourine (F<sub>2</sub>) easily, and that F<sub>2</sub> could serve as the precursor (preliminary, original) gas that, like CF<sub>4</sub>, can be converted into CF<sub>3</sub>, CF<sub>2</sub>, 2F, etc. On the other hand, we should carefully observe the CO within the COF<sub>2</sub>, as CO may lower the selectivity.

## Experiment Results

We compared the etching performance of COF<sub>2</sub>, CF<sub>4</sub>, and CHF<sub>3</sub>, both on SiO<sub>2</sub> films and SiN films. Samco’ s ICP Etching System, the RIE-200iP, was used in this experiment. The etching rate, selectivity, and surface smoothness were evaluated and are shown in Tables 2 and 3.

CF<sub>4</sub> showed the highest etch rate on the SiO<sub>2</sub> film, and the etch rates of COF<sub>2</sub> and CHF<sub>3</sub> on SiO<sub>2</sub> film were close. On the other hand, CHF<sub>3</sub> showed the best selectivity, as it will break down into carbon hydride) CH components, while COF<sub>2</sub> showed the worst result because it contained oxygen. Surfaces were smooth and no difference among the three gas processes was observed. Etch profiles cannot be evaluated quantitatively, but a selectivity of 1:1 or better suggests that all gases work well in transferring the mask shape onto SiO<sub>2</sub>.

We achieved similar results to SiO<sub>2</sub> film etching experiments in SiN film etching, except that CHF<sub>3</sub> attained a significantly lower etch rate. The possible causes were disruption by hydrogen atoms and deposition by carbon hydride molecules

(CH). COF<sub>2</sub> and CF<sub>4</sub> showed close selectivity, and CHF<sub>3</sub> showed the lowest selectivity among the three gases. We observed no significant difference in surface smoothness and etch profile like the previous experiment on the SiO<sub>2</sub> films.

## Conclusion

Samco has executed experiments to see whether or not COF<sub>2</sub> can serve as an alternative to CF<sub>4</sub> and CHF<sub>3</sub>, which are global warming gases, and has concluded that COF<sub>2</sub> is not necessarily inferior to CF<sub>4</sub> and CHF<sub>3</sub> as an etching gas for SiO<sub>2</sub> and SiN. We learned that the selectivity in SiO<sub>2</sub> and SiN etching by COF<sub>2</sub> can be improved by adding hydrogen (H<sub>2</sub>) and methane (CH<sub>4</sub>) to the experiment of SiO<sub>2</sub> etching by CHF<sub>3</sub>, and believe that COF<sub>2</sub> works well as an etching gas for SiO<sub>2</sub> etching and SiN etching. However, we should pay attention to the characteristics that result when COF<sub>2</sub> reacts with some metals and water.

Table 1. GWP (Global Warming Potential) data sheet [1]

Gas	GWP 100yr
CO <sub>2</sub>	1
CH <sub>4</sub>	25
N <sub>2</sub> O	298
SF <sub>6</sub>	22,800
NF <sub>3</sub>	17,200
CF <sub>4</sub> (PFC-14)	7,390
C <sub>2</sub> F <sub>6</sub> (PFC-116)	12,200
C <sub>3</sub> F <sub>8</sub> (PFC-218)	8,830
CHF <sub>3</sub> (HFC-23)	14,800
CH <sub>2</sub> F <sub>2</sub> (HFC-32)	675
COF <sub>2</sub>	1 [2]

Table 2. SiO<sub>2</sub> Etching Results

Gas	Etch Rate (nm/min)	Selectivity (SiO <sub>2</sub> /PR)	Surface
COF <sub>2</sub>	130.4	1.23	Good
CF <sub>4</sub>	165.2	1.69	Good
CHF <sub>3</sub>	130.0	2.96	Good

Table 3. SiN Etching Results

Gas	Etch Rate (nm/min)	Selectivity (SiN/PR)	Surface
COF <sub>2</sub>	127.0	1.11	Good
CF <sub>4</sub>	153.0	1.23	Good
CHF <sub>3</sub>	87.0	1.09	Good

### References

[1] IPCC Fourth Assessment Report (AR4)

[2] Energy and Industrial Technology Development Organization (NEDO)