Technical-Report

SiO_2 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_2), which has lower global warming potential (GWP) than tetrafluoromethane (CF_4) and trifluoromethane (CHF_3).

Introduction

CF_4 and CH_3 gases are commonly used in dry etching of silicon dioxide (SiO_2) 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_2 as an alternative to CF_4 and CH_3.

COF_2 was developed in New Energy and Industrial Technology Development Organization (NEDO) project as an alternative to PFC. Some researchers reported that COF_2 was used to clean the chambers after Chemical Vapor Deposition (CVD), but COF_2' s use in etching has not been reported yet. We discovered that COF_2 can etch SiO_2 film, as it can function as a cleaning gas following CVD. Additionally, SAMCO has determined that COF_2 could be broken down into carbon monoxide (CO) and Flourine (F_2) easily, and that F_2 could serve as the precursor (preliminary, original) gas that, like CF_4, can be converted into CF_3, CF_2, 2F, etc. On the other hand, we should carefully observe the CO within the COF_2, as CO may lower the selectivity.

Experiment Results

We compared the etching performance of COF_2, CF_4, and CHF_3, both on SiO_2 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_4 showed the highest etch rate on the SiO_2 film, and the etch rates of COF_2 and CHF_3 on SiO_2 film were close. On the other hand, CHF_3 showed the best selectivity, as it will break down into carbon hydride) CH components, while COF_2 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_2.

We achieved similar results to SiO_2 film etching experiments in SiN film etching, except that CHF_3 attained a significantly lower etch rate. The possible causes were disruption by hydrogen atoms and deposition by carbon hydride molecules (CH). COF_2 and CF_4 showed close selectivity, and CHF_3 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_2 films.

Conclusion

SAMCO has executed experiments to see whether or not COF_2 can serve as an alternative to CF_4 and CHF_3, which are global warming gases, and has concluded that COF_2 is not necessarily inferior to CF_4 and CHF_3 as an etching gas for SiO_2 and SiN. We learned that the selectivity in SiO_2 and SiN etching by COF_2 can be improved by adding hydrogen (H_2) and methane (CH_4) to the experiment of SiO_2 etching by CHF_3, and believe that COF_2 works well as an etching gas for SiO_2 etching and SiN etching. However, we should pay attention to the characteristics that result when COF_2 reacts with some metals and water.

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

Gas		GWP 100yr
CO_2		1
CH_4		25
N_2O		298
SF_6		22,800
NF_3		17,200
CF_4	(PFC-14)	7,390
C_2F_6	(PFC-116)	12,200
C_3F_8	(PFC-218)	8,830
CHF_3	(HFC-23)	14,800
CH_2F_2	(HFC-32)	675
COF_2		1 [2]

Table 2. SiO_2 Etching Results

Gas	Etch Rate (nm/min)	Selectivity (SiO_2/PR)	Surface
COF_2	130.4	1.23	Good
CF_4	165.2	1.69	Good
CHF_3	130.0	2.96	Good

Table 3. SiN Etching Results

Gas	Etch Rate (nm/min)	Selectivity (SiN/PR)	Surface
COF_2	127.0	1.11	Good
CF_4	153.0	1.23	Good
CHF_3	87.0	1.09	Good

References
[1] IPCC Fourth Assessment Report (AR4)
[2] Energy and Industrial Technology Development Organization (NEDO)