技術報告

Green NF_3^{TM} の開発
－添加ガスによるコスト削減,環境負荷削減効果の検討－

Development of Green NF_3^{TM}
-Lowering the Cost and Environmental Impact of NF_3 through the Use of Additives-

MITCHELL Glenn* SUBRAMANIAN Ramkumar* WYSE Carrie*
SEYMOUR Adam* GARDINER Robin* TORRES Robert*

我々はクリーニングプロセスに使用される NF_3 ガスの利用効率を向上することによって,NF_3 ガスの使用量を削減できる Green NF_3^{TM} を開発した。NF_3 ガスに CO_2 を添加したガスを導入し,リモートプラズマ源を用いてクリーニング活性種を形成した。この手法により形成したクリーニング活性種により,クリーニングの効率を維持または向上しながら,量産装置での NF_3 使用量が 10%削減可能となった。本稿では,Green NF_3^{TM} の開発成果として,社内評価と量産装置評価（OEM ベータテスト）の結果を記述する。また,スループット向上のための取り組みについても言及する。

We have developed Green NF_3^{TM}, with the objective of reducing the amount of NF_3 used in a cleaning process as well as to improve the utilization of NF_3 in the process. This is achieved by introducing a CO_2 additive into the NF_3 which forms in-situ cleaning species in the remote plasma source that are more effective than the NF_3 by itself. Using this approach, the amount of NF_3 can be reduced by up to 10% on an original equipment manufacturer (OEM) tool. This paper discusses the development and results obtained with Green NF_3 technology during both in-house laboratory feasibility studies and OEM tool beta tests. Insights into approaches for improving the throughput are also provided.

1. Introduction

NF_3 is traditionally used in chemical vapor deposition (CVD) chamber cleaning processes for silicon semiconductors. However, the largest use of NF_3 is in the manufacture of thin film transistor (TFT) displays, where the cost of NF_3 is a significant portion of the non-capital cost structure of the fab. Reduction in the usage of NF_3 for flat panel display chamber cleaning would therefore have a large impact on the running expenses and profitability of many fabs.

Additionally, as the semiconductor industry moves to more stringent regulations regarding high global warming potential (GWP) gases, NF_3 usage and emissions are coming under scrutiny. A recent report estimates that NF_3 has a GWP impact of 17,000 CO_2 equivalents, which make the molecule a very high potential contributor to global warming over other gases used in the semiconductor industry[1)].

Our concept and feasibility experiments have established that the addition of CO_2 to NF_3, called Green NF_3™, can reduce the amount of NF_3 needed in a cleaning process while maintaining the cleaning rate. Tests were also conducted at a customer site on a TFT plasma enhanced CVD (PECVD) tool, demonstrating the real-world benefits of Green NF_3™.

Overall, the environmental impact of NF_3 usage is lessened through better utilization of NF_3 radicals and fragments as a result of the addition of CO_2. The better utilization of NF_3 in the process significantly reduces the amount of NF_3 molecules in the process emissions.

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* Advanced Technology Center, Matheson Tri-gas Inc., Longmont, Colorado, USA

2. Theory

Ideas behind better utilization and/or reduction of NF_3 in a cleaning process revolve around the complexation of other molecules and molecular fragments to create new in-situ cleaning molecules that are otherwise difficult to deliver due to packaging stability or toxicity issues.

CO_2 was chosen as the first NF_3 additive, due to it's simplicity of use and fragmentation in a plasma. Fig. 1 shows the concept and theory of the Green NF_3 chemistry. Fragmentation of NF_3 and the CO_2 additive in the plasma results in the production of CO and F radicals. These then react further to generate in-situ COF and COF_2 species that have enhanced cleaning properties.

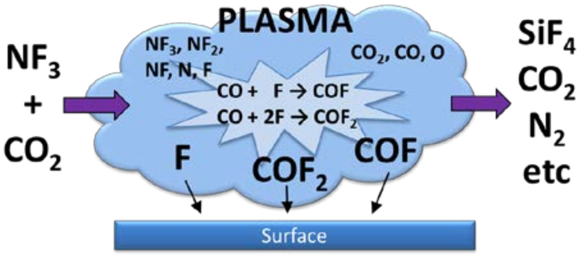

Fig. 1. Illustrative theory behind Green NF_3™ NF_3 + CO_2 fragment reactions

COF_2 has already been studied[2,3,4)] as a potential replacement for Perfluorocarbon (PFC) and NF_3 chamber cleaning gases because it has low GWP and no ozone depletion potential. Acceptance by the industry has been slow however because of the high gas cost and the high capital cost of additional environment, safety and health (ESH) controls that are required because of the toxicity of COF_2[5)].

Our success in generating COF_2 inside the chamber where it is needed is a great improvement and allows the industry to use the cleaning capabilities of this material without the additional concerns of safety and cost[6)].

3. Feasibility Experiments

Experiments were conducted in a home-built Hastelloy chamber fitted with a remote plasma system and using dilute mixtures of NF_3 and CO_2 in argon. Various substrates were placed in the chamber and etched to determine the effectiveness of the different NF_3 and CO_2 ratios in the plasma. Ex-situ fourier transform infrared spectroscopy (FTIR) of the chamber effluent was peformed to determine the active species in the plasma and chamber. Fig. 2 shows a schematic diagram of the experimental set-up. For the feasibility experiments, total argon flow was kept at 2.5 slpm in order to keep the plasma conditions constant. Typical process chamber pressure was 2 Torr and the plasma power was kept at 2.6 kW. NF_3 and CO_2 flows were varied in the argon plasma to test the effect of the CO_2:NF_3 ratio on the etch rate of various substrates.

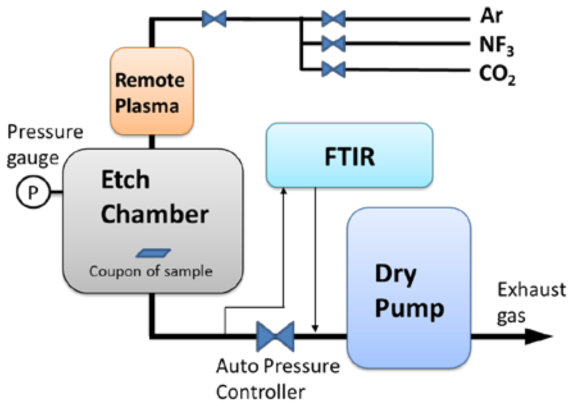

Fig. 2. Set-up used for feasibility experiments

Coupons of SiO_2 wafer samples (Boron Phosphorus silicate glass (BPSG) or Tetraethyl orthosilicate (TEOS) were used for the etch tests. The coupons were placed in the chamber and then cleaning gas, which was activated by the remote plasma system under set conditions of composition, flow and pressure, etched the sample wafer. The etch rate was determined by process time and film thickness measurement using a reflectometer and profilometer.

In order to understand the CO_2/NF_3 reaction chemistry in more detail, laboratory feasibility experiments were carried out to investigate (a) the etch rate versus CO_2 addition to NF_3 and (b) the concentration of NF_3 and other gases in the chamber emisisons. As shown in Fig. 3 adding CO_2 to the NF_3 pre-plasma at a CO_2:NF_3 ratio of 0.75:1 resulted in a higher etching rate than using just NF_3 alone.

Results of FTIR measurements of the COF_2 and NF_3 concentrations in the chamber emissions when different CO_2:NF_3 ratios were used in the chamber are shown in Fig. 4. At a CO_2: NF_3 ratio of 0.75:1 a large reduction in NF_3 was observed in the emissions and this was accompanied by an associated increase in formation of COF_2.

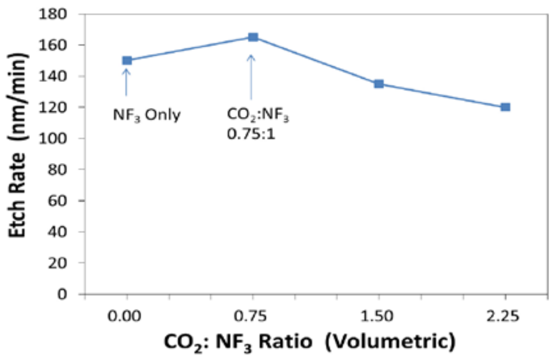

Fig. 3. Effect of CO_2 on NF_3 BPSG etch rates

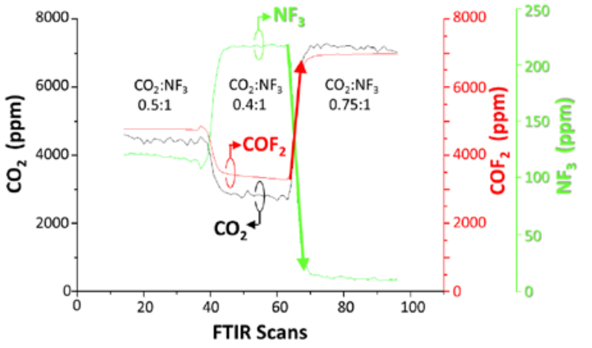

Fig. 4. Reduction in NF_3 emissions with addition of CO_2 measured by FTIR, during the etching of a SiO_2 (TEOS) surface

We therefore conclude from these feasibiity studies that (a) the cleaning rate can be maintained or improved by adding CO_2 to the NF_3 and (b) that the improved cleaning rate and reduced NF_3 level in the chamber emissions are due to in-situ formation of COF_2.

4. OEM PECVD Tool Testing

After demonstrating initial success on a diluted scale, the Green NF_3™ (NF_3 + CO_2 mixture) was tested at a customer site on an OEM TFT PECVD tool.

A 300 nm silicon nitride layer was deposited inside the PECVD chamber and varying amounts of NF_3 and CO_2 were added to test the effect on the clean time of the chamber. The NF_3 + CO_2 mixture was tested pre-plasma at a flow of 20 slpm and the NF_3 was replaced with CO_2 up to 20%. The tests were performed with a sub-atmospheric in-situ FTIR to analyze the gases present. The etching rate and cleaning end point was determined by measuring the pressure change from the species produced in the chamber and by a visual check (color change of chamber surface) made via a chamber view port. Fig. 5 shows the etch rate as NF_3 was replaced by CO_2. No change in etch/clean rate was observed with up to 10% replacement of NF_3 with CO_2, within the measurement error.

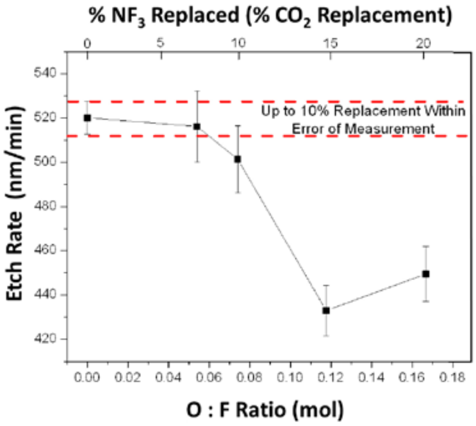

Fig. 5. Etch rate/clean time results on PECVD tool as NF_3 is increasingly replaced with CO_2

Fig. 6 shows the generation of in-situ COF_2 by NF_3 + CO_2 in the remote plasma source under different conditions. At the condition of 7.5% replacement of NF_3, NF_3 emissions are clearly the lowest as compared to just a linear decrease in NF_3 concentration, which is also shown Fig. 6. This indicates that the cleaning species has been efficiently converted from available NF_3 that is not already being consumed in the chamber cleaning process. It is also evident that the COF_2 concentration increases linearly with CO_2 replacement. Although the active species may not be the emitted species due to consumption in the chamber, it is reasonable to assume that COF_2 is one of the main active species based on our feasibility study. The highest efficiency condition is achieved by maximizing the active species from NF_3 and COF_2.

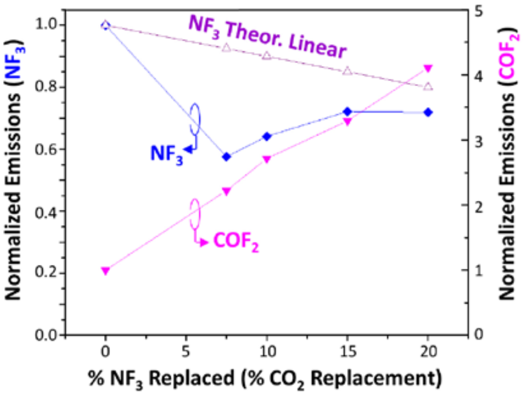

Fig. 6. Creation of in-situ COF_2 as observed by in-situ FTIR during Green NF_3™ experiments on PECVD tool

Fig. 7 shows how a response surface plot can be used to optimize the etch rate, percentage NF_3 replaced and the NF_3 tool emissions. The lowest NF_3 emission is around 10% CO_2 replacement. At this point in the response curve the etch rate is maintained at 520 nm/min and the NF_3 emissions are also minimized. Some differences in NF_3 emissions were observed between the feasibility data and OEM tool tests and this is due to the different conditions used in the two experiments. However, monitoring NF_3 emissions and chamber cleaning rates, the process chamber conditions can be optimized for the amount of CO_2 that can replace NF_3 in the process.

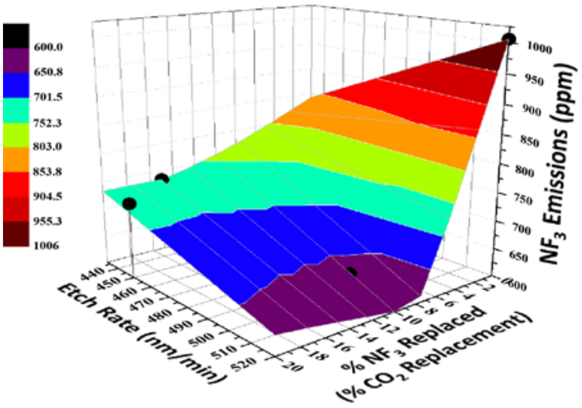

Fig. 7. Response surface of etch rate, NF_3 emissions and % NF_3 replaced with CO_2

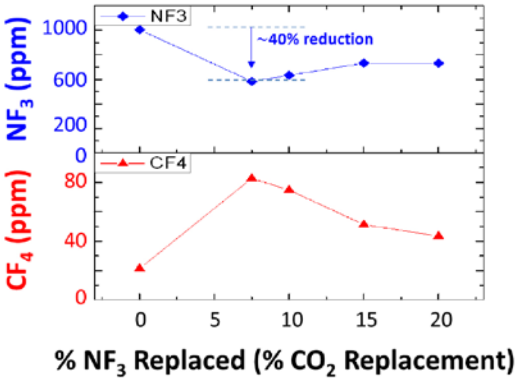

Fig. 8. Change in effluent species during pre-plasma CO_2 addition to NF_3 on PECVD tool

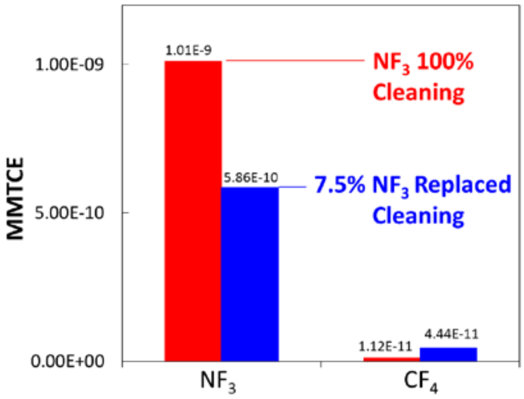

Fig. 9. Million Metric Tons of Carbon Equivalence (MMTCE) evaluation for the optimized condition

Fig. 8 shows NF_3 and CF_4 emission concentrations as a function of NF_3 replaced by CO_2. It should be noted that the effluent species were measured directly off the process chamber upstream of the pumping system and subsequent inert gas dilutions. With NF_3 only as the cleaning process gas, 1000 ppm NF_3 was observed in the tool emissions. On the other hand, when NF_3 was replaced with 7.5% CO_2, the NF_3 concentration in the outlet emissions dropped to 600 ppm. It was noted that CF_4 levels did increase as CO_2 was added, but the CF_4 concentration was relatively low. Therefore, the Green NF_3^{TM} process enables ~40% NF_3 emissions reduction directly from the process chamber, which greatly impacts the Million Metric Tons of Carbon Equivalence (MMTCE) as shown in Fig. 9. The MMTCE is a gauge for evaluating global warming potential gas emissions.

In summary we have evaluated Green NF_3^{TM} on an OEM PECVD tool and successfully demonstrated high efficiency cleaning while replacing NF_3 with 10% CO_2. Maintaining a constant etch/clean rate while using less NF_3 is a major advantage of the approach. However the added benefit of reducing NF_3 emissions by 40% is also very beneficial from an environmental standpoint.

5. Future Directions to Improve Green NF_3

Green NF_3^{TM} is a unique technology to generate in-situ active etching species for chamber cleaning. However, the method is limited to 10% NF_3 usage reduction in order to maintain the etch/clean rate. As the market demands for increased performance continue to drive developments, there have been calls for greater NF_3 reduction with higher etch rates in order to realize high throughput and lower costs. We are currently working on improving Green NF_3^{TM}. One of the approaches is to compensate F species by adding a more cost effective PFC gas together with the CO_2. This is done to maximize COF_2 species and reduce NF_3 usage further. Although PFC gases also have global warming properties, they are typically lower than NF_3 and may be decomposed effectively if plasma/reaction conditions are optimized. We believe in the future a new cleaning process with high performance, low cost and low emission gas can be developed.

References

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