Analysis of Variables Effects in 300mm PECVD Chamber Cleaning Process Using NF_3

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ABSTRACT

NF_3, Chamber cleaning gas, has a high Global Warming Potential (GWP) of 17,000, causing significant greenhouse effects. Reducing gas usage during the cleaning process is crucial while increasing the cleaning Rate and reducing cleaning standard deviation (Stdev). In a previous study with a 6-inch PECVD chamber, a multiple linear regression analysis showed that Power and Pressure had no significant effect on the cleaning Rate because of their P-values of 0.42 and 0.68. The weight for Flow is 11.55, and the weights for Power and Pressure are 1.4 and 0.7. Due to the limitations of the research equipment, which differed from those used in actual industrial settings, it was challenging to assess the effects in actual industrial environment. Therefore, to show an actual industrial environment, we conducted the cleaning process on a 12-inch PECVD chamber, which is production-level equipment, and quantitatively analyzed the effects of each variable. Power, Pressure, and NF3 Flow all had P-values close to 0, indicating strong statistical significance. The weight for Flow is 15.68, and the weights for Power and Pressure are 4.45 and 5.24, respectively, showing effects 3 and 7 times greater than those with the 6-inch equipment on the cleaning rate. Additionally, we analyzed the cleaning Stdev and derived that there is a trade-off between increasing the cleaning Rate and reducing the cleaning Stdev.

Key Words : Eco-friendly, PECVD, Dry-Cleaning, Multiple Linear Regression, ANOVA, QMS, NF_3

1. Introduction

As semiconductor devices become more miniaturized, the importance of the cleaning process is increasingly emphasized [1]. The thin films formed through deposition processes adhere not only to the wafer but also to the entire interior of the chamber, which can shorten the equipment's lifespan and cause wafer contamination in subsequent processes, leading to quality issues [2]. Therefore, periodic cleaning of the chamber is essential to reduce defect rates in subsequent processes and to prevent corrosion and weakening of the equipment, thereby extending its lifespan. Chamber cleaning is primarily done using fluorine-containing gases, and a dry-cleaning process is used to minimize downtime [3]. Before environmental regulations, SF_6 was mainly used as a cleaning gas, but after the regulations, it was replaced by NF_3 [4,5]. NF_3 has a high etch rate and etch efficiency [6,7], but with a GWP of about 17,000, it has a significant environmental impact even in small amounts. Also, NF_3 is expected to be included in future regulations as it has been designated as the seventh greenhouse gas during the second commitment period of the Kyoto Protocol [8]. Nevertheless, NF_3 is used in all cleaning processes in the semiconductor

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industry, and its usage continues to increase. To address these issues, it is necessary to develop a gas to replace NF_3 or to improve process efficiency [9]. Currently, various alternative chamber cleaning gases are being verified and developed, but there are limitations in applying these gases to current industrial environment [10]. Therefore, it is crucial to quantify the effects of process variables to operate the process efficiently.

In the current semiconductor industry, 12-inch wafers have become the standard. Therefore, conducting experiments using 12-inch equipment is essential to adhere to industry standards and maintain competitiveness in the market. However, due to difficulties in using this equipment, many studies have used 6-inch equipment. These limitations have made it challenging to accurately understand the actual industrial environment. Thus, this study aims to apply the techniques and methodologies developed on 6-inch equipment to 12-inch equipment to suggest directions for improving efficiency. Recent cleaning experiments conducted in a 6-inch PECVD (Plasma Enhanced Chemical Vapor Deposition) chamber showed that the effects of Power and Pressure were not significant, but there were limitations in assessing the effects due to the scale difference from the equipment used in actual industry [11]. In actual industry, the cleaning process is conducted using remote plasma on 12-inch equipment. Therefore, to understand the effects of variables in an actual industrial environment, we revalidated the experiments of previous studies using a production-level 12-inch PECVD equipment. We analyzed the effects of cleaning process variables and derived the correlation between process variables and the environmental impact of exhaust gases by analyzing the exhaust gases using QMS (Quadruple Mass Spectrometer) data. Additionally, since small particles adhering to the chamber walls can affect subsequent processes, it is important that the entire chamber is cleaned effectively [12]. Therefore, we analyzed not only the cleaning rate but also the changes in standard deviation (Stdev) over a broader range using 12-inch wafers.

2. Experiment Setup

2.1 Design of Experiment

Using the statistical software Minitab, a Central Composite Design (CCD) experiment was designed. Central Composite Design designs a first-order model through 2^N factorial experiments at the corner points and a second-order model relationship between the response variables and predictor variables through 2N+1 star points. The process variables were set to power, pressure, and gas flow rate for comparative verification with a previous study [11]. The low and high values of the star points for Power, Pressure, and flow rate were specified, while other variables were fixed as shown in the Table 1. The recipes used in the experiment are summarized in the following Table 2.

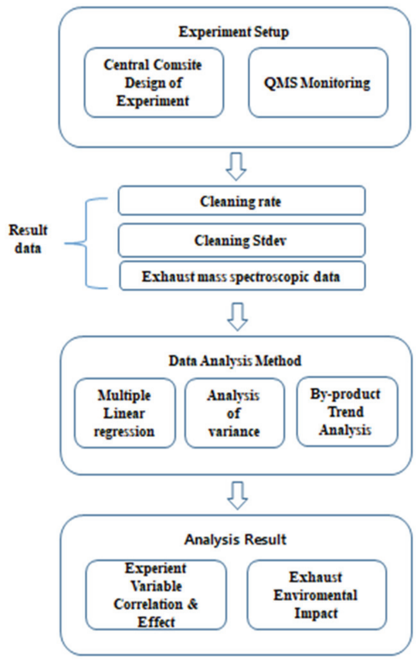


Fig. 1. Research scheme with a topical and conceptual flow chart.

Table 1. Central Composite Design Recipe

CCD Star Point	Low Level	High Level
RPS Power(W)	2250	2750
Pressure(mTorr)	2500	3500
NF_3(sccm)	1500	2500
Ar(sccm)	2500	
w/Temp(℃)	200	
Time(sec)	15	

Table 2. The CCD'3 Design Table of Experiment

Standard Run	RPS Power(W)	Pressure(mTorr)	NF_3(sccm)
1	Level -0.6	Level -0.6	Level -0.6
2	Level 0.6	Level -0.6	Level -0.6
3	Level -0.6	Level 0.6	Level -0.6
4	Level 0.6	Level 0.6	Level -0.6
5	Level -0.6	Level -0.6	Level 0.6
6	Level 0.6	Level -0.6	Level 0.6
7	Level -0.6	Level 0.6	Level 0.6
8	Level 0.6	Level 0.6	Level 0.6
9	Level -1	Level 0	Level 0
10	Level 1	Level 0	Level 0
11	Level 0	Level -1	Level 0
12	Level 0	Level 1	Level 0
13	Level 0	Level 0	Level -1
14	Level 0	Level 0	Level 1
15	Level 0	Level 0	Level 0
16	Level 0	Level 0	Level 0
17	Level 0	Level 0	Level 0
18	Level 0	Level 0	Level 0
19	Level 0	Level 0	Level 0
20	Level 0	Level 0	Level 0

2.2 12-inch PECVD Chamber

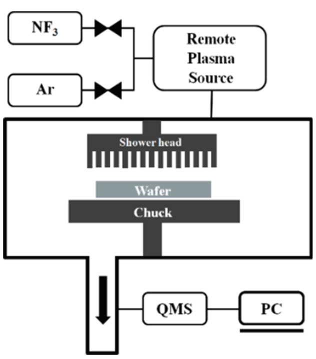


Fig. 2. Experimental apparatus of 13.56MHz PECVD system for SiO_2 cleaning.

The PECVD chamber used in the experiment is a 12-inch production-level PECVD chamber from TES, located at the Semiconductor Process Diagnostics Lab at Myongji University. It is equipped with a 1kW RF Power Generator operating at 13.56 MHz and an Auto Impedance Matching Unit on top. Additionally, it has an NF_3 RPS from Advanced Energy and a QMS sensor placed at the chamber exhaust.

2.3 QMS(Quadruple Mass Spectrometer)

For QMS equipment, we used the equipment from ATIK. QMS is a device that measures residual gases within a vacuum system and was used to monitor and analyze changes in reactive and generated gases within the process system. QMS is divided into three parts: Ion Source, Mass Filter, and Detector. In the ion source, thermo electrons are emitted from a filament to ionize the gas. The ionized cations are separated in the mass filter according to their mass-to-charge ratio. The separated cations are measured by the detector and displayed as current values.

2.4 Cleaning Rate and Cleaning Stdev

The cleaning rate, which indicates the degree of cleaning, and the cleaning Stdev, which indicates the difference in the degree of cleaning, were measured using a Reflectometer.

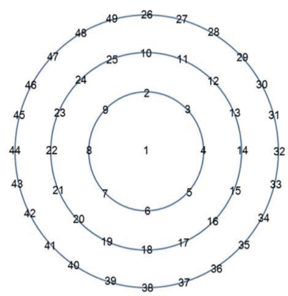


Fig. 3. 12-inch wafer map location number.

49 points were set on a 12-inch wafer, and the oxide thickness before and after cleaning at each point was measured. The average Cleaned Thickness was divided by the cleaning time to define the degree of cleaning per unit time as the cleaning rate, and the standard deviation of the Cleaned Thickness at the 49 points was defined as the cleaning Stdev.

$$\textit{Cleaning Rate}(\text{Å/sec}) = \frac{\sum_{i=1}^{49} t_i}{49} \ / \ \text{Cleaning time} \quad (1)$$

$$\textit{Cleaning Stdev}(\text{Å}) = \sqrt{\frac{\sum_{i=1}^{49}(t_i-\bar{t})^2}{49}} \quad (2)$$

t_i: Oxide Thickness at point i

$\bar{t}$: 49point Average Oxide Thickness

Twenty samples with 7000 Å of SiO_2 deposited were prepared for the chamber cleaning process. The cleaning rate in this paper refers to the chamber cleaning rate, and the cleaning Stdev refers to the difference in the degree of cleaning according to the location within the chamber. Although it might be more accurate to evaluate the cleaning rate and Stdev by opening the chamber and examining the chamber walls before and after the dry-cleaning process, due to various constraints, the wafer placed on the chuck was used as a proxy for the chamber's inner walls for the experiment.

3. Result and Discussion

3.1 Chamber Cleaning Process Results

Reproducibility is the property where measured results consistently appear, and it is one of the core principles of the scientific method. Fig. 4 shows the reproducibility results. In this study, reproducibility was confirmed under Level 0 conditions for the variables. Under these conditions, the cleaning rate and cleaning Stdev showed error margins within a maximum of 6% and 5%, respectively.

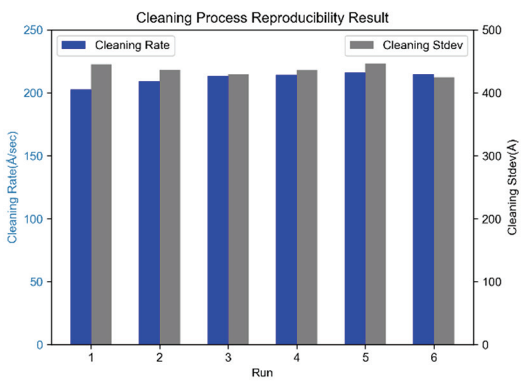
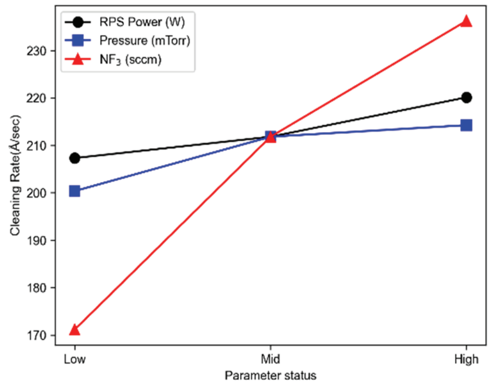
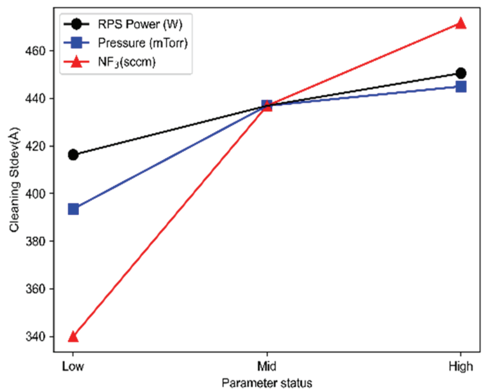


Fig. 4. Cleaning Process Reproducibility Result.

The results of the NF_3 cleaning process using the three process variables power, pressure, and gas flow rate are shown in fig. 5. To evaluate the level changes of specific variables, the other variables were fixed at Level 0 conditions. The experimental results showed that all three variables had the highest cleaning rate and cleaning Stdev at high values. As power and pressure increased, the cleaning rate also increased, with the most noticeable increase occurring when the flow rate increased. When each variable level changed from Level -1 to Level 0, and from Level 0 to Level 1, the rate of increase gradually decreased.



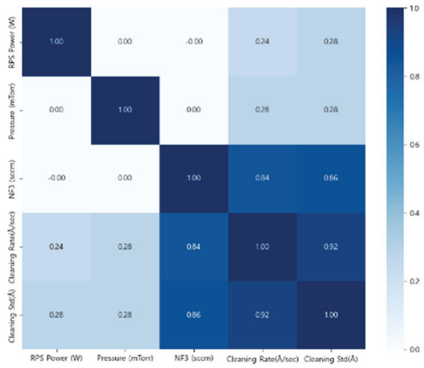
(a)



(b)

Fig. 5. (a) Cleaning rate and (b) Cleaning Stdev result according to process parameter variations.

To quantitatively understand the relationship between variables, cleaning rate, and cleaning Stdev, Pearson correlation analysis was conducted. The Pearson correlation coefficient quantifies the linear correlation between two variables. The analysis results shown in Fig. 6 indicate a very strong positive correlation between cleaning rate and NF_3 flow rate, with a correlation coefficient of 0.84. Power and pressure showed small positive correlations of 0.24 and 0.28, respectively. This suggests that flow rate is closely related to the cleaning rate. Power and pressure also showed positive correlations, indicating that the optimal settings of these two variables can positively impact the cleaning rate.



Scale of correlation coefficient coefficient	Value
0<r<0.2	**Very Low Correlation**
0.2<r<0.4	**Low Correlation**
0.4<r<0.6	**Moderate Correlation**
0.6<r<0.8	**High Correlation**
0.8<r<1.0	**Very High Correlation**

Fig. 6. Correlation coefficient of cleaning rate and cleaning Stdev.

For cleaning Stdev, flow rate also showed a very strong positive correlation with a coefficient of 0.86. This indicates that flow rate is closely related not only to cleaning rate but also to cleaning Stdev. Power and pressure showed small positive correlations of 0.28 each. Therefore, it is expected that the combination of power and pressure can help reduce cleaning Stdev.

Fig. 7 shows the cleaning rate and Stdev according to the flow rate through a contour map. As confirmed by the wafer map, there is a simultaneous increase in both the cleaning rate and standard deviation.

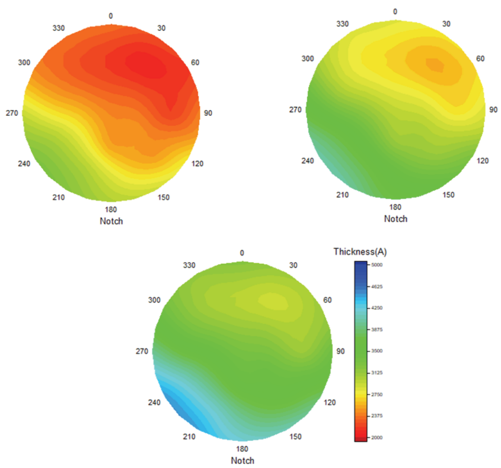


Fig. 7. Cleaned Thickness contour map of the SiO_2 film with the remote plasma dry-Cleaning process.

To investigate the effects of process variables on cleaning rate and Stdev, RSM (Response Surface Modeling) was derived, but the quadratic effects were not significant. Therefore, a multiple linear regression model was used to analyze the impact of each variable.

3.2 Multiple Linear Regression

Multiple linear regression is a linear model that explains the relationship between independent variables X and dependent variable Y by determining the weights of each variable and identifying the significant variables that have a meaningful impact on the dependent variable. When the dependent variable Y is influenced by several independent variables X_1, X_2, …, X_P, the relationships among these variables are modeled. In this study, the independent variables $X1$, $X2$, $X3$ were defined as Power, Pressure, and Flow, respectively, and the dependent variables $Y1$ and $Y2$ were defined as cleaning rate and cleaning Stdev. Two separate multiple linear regression analyses were conducted.

Table 3. Selection Dependent and Independent variables

Dependent Variables	Independent Variables		
$Y_{C/R}$	X_{Power}	$X_{Pressure}$	X_{Flow}
Y_{Stdev}	X_{Power}	$X_{Pressure}$	X_{Flow}

3.2.1 Cleaning Rate Analysis

The evaluation of the fit of the multiple linear regression model resulted in an R^2 score of 84%, indicating a high level of fit. A high R^2 score indicates that the regression model effectively explains the relationship between the predictor variables and the dependent variable. The p-value of the regression model was close to 0, indicating that the predictor variables in the model are very effective in explaining the variation in the dependent variable. Because the p-value is smaller than the commonly used significance level of 0.05, this model is statistically significant.

The multiple linear regression analysis results confirmed that Power, Pressure, and Flow all had P-values close to 0, indicating statistical significance. The detailed statistics of the model are summarized in Table 4. Flow had the highest weight of approximately 15.68, Power had a weight of 4.45, and Pressure had a weight of 5.24. Previous research showed that the effects of power and pressure were not significant in the cleaning process, with weights of 1.4 and 0.7, respectively, compared to the most significant variable, Flow, which had a weight of 11.55[11]. However, in our experiment, the effects of power and pressure were very significant, showing three and seven times the effect on cleaning rate compared to previous research. This indicates that by reducing the amount of NF_3 gas and optimizing power and pressure, the cleaning rate can be increased while simultaneously reducing greenhouse gas emissions.

Table 4. Statistical Parameter Regarding The Multiple Linear Regression Model

Variables	Coef	Std Err	t	P>|t|
RPS Power(W)	4.445	1.803	2.465	0.025
Pressure(mTorr)	5.236	1.803	2.903	0.010
NF_3(sccm)	15.679	1.803	8.694	0.000
Constant	206.656	1.803	114.593	0.000

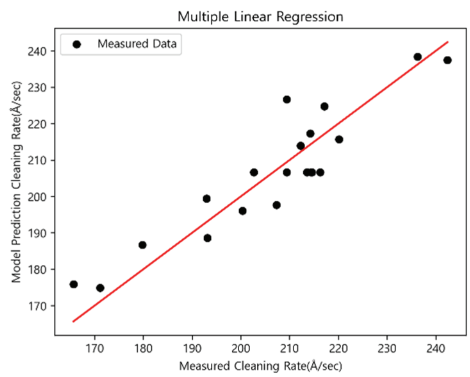


Fig. 8. Prediction result obtained by multiple linear regression.

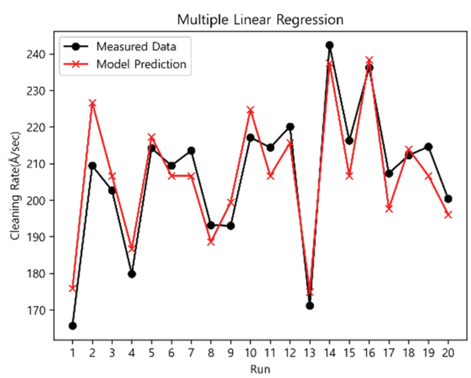


Fig. 9. Graphical comparison of the actual and predicted values.

3.2.2 Cleaning Stdev Analysis

A multiple linear regression analysis was also performed on cleaning Stdev. This model had an R^2 score of 90%, indicating a high level of fit, and the p-value was close to 0, making it statistically significant. cleaning Stdev is an important variable to maintain process consistency. Since very small particulate residues from the cleaning process can affect subsequent processes, it is crucial that all areas within the chamber are cleaned evenly. Therefore, lower cleaning Stdev is better.

Table 5. Statistical Parameter Regarding The Multiple Linear Regression Model.

Variables	Coef	Std Err	t	P>|t|
RPS Power(W)	10.860	3.122	3.479	0.003
Pressure(mTorr)	11.069	3.122	3.546	0.003
NF_3(sccm)	33.373	3.122	10.690	0.000
Constant	425.131	3.122	136.177	0.000

The multiple linear regression analysis results confirmed that Power, Pressure, and Flow all had P-values close to 0, indicating statistical significance. Flow also had the highest weight of approximately 33.37 for cleaning Stdev, Power had a weight of 10.86, and Pressure had a weight of 11.07. These results demonstrate a trade-off relationship among the three variables regarding cleaning rate and Stdev, indicating that precise adjustment of power and pressure is necessary to optimize the cleaning process. The detailed statistics of the model are summarized in Table 5.

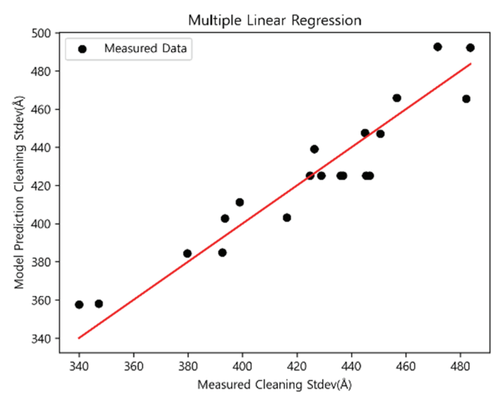


Fig. 10. Prediction result obtained by multiple linear regression.

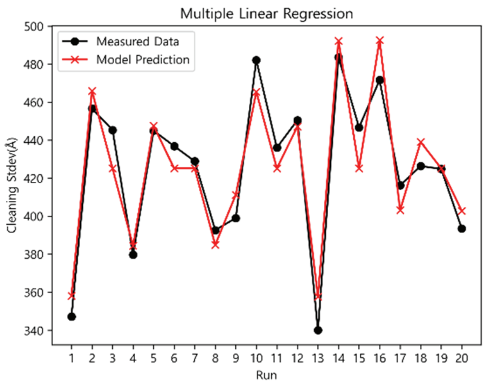


Fig. 11. Graphical comparison of the actual and predicted values.

These analysis results indicate that Flow is the variable that has the greatest impact on both cleaning rate and Stdev. By appropriately adjusting power and pressure, process efficiency can be improved. This data can be used as important information for optimizing cleaning processes in the semiconductor industry.

3.3 By-product Monitoring

The reactions generating F radicals from NF_3 during the cleaning process are represented by equations (3) and (4), and the chemical reaction where the generated F radicals remove the oxide film in the chamber is shown in equation (5). The presence of F, NF_2^+, and SiF_3^+ measured through QMS plays an important role in understanding the efficiency and environmental impact of the cleaning process. The main by-products and peaks of the cleaning process are shown in Table 6 and Fig. 12.

$$e + NF_3 \rightarrow e + NF_2 + F \tag{3}$$

$$NF + NF_2 \rightarrow N_2 + F_2 + F \tag{4}$$

$$SiO_2(s) + 4F(g) \rightarrow SiF_4(g) + O_2(g) \tag{5}$$

The detection of SiF_3^+ is directly related to the cleaning rate, indicating the effectiveness of the cleaning process and helping determine the progress of the process.

NF_2^+ is produced when NF_3 ionizes and one fluorine atom is released. NF_2^+ that is not completely dissociated during the process recombines with fluorine atoms in the chamber and is emitted as NF_3. Also, NF_3 that does not directly participate in the cleaning process is emitted is also measured as NF_2^+ through QMS. Therefore, the peak of NF_2^+ observed in QMS represents waste gas that does not participate in the reaction, which can contribute to the greenhouse effect and reduce the efficiency of the cleaning process.

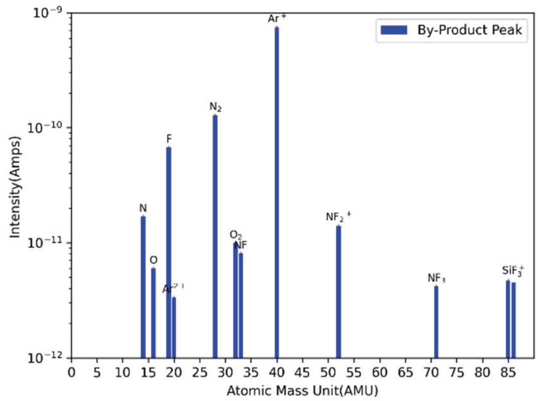


Fig. 12. QMS spectrum during SiO_2 chamber cleaning using NF_3 plasma.

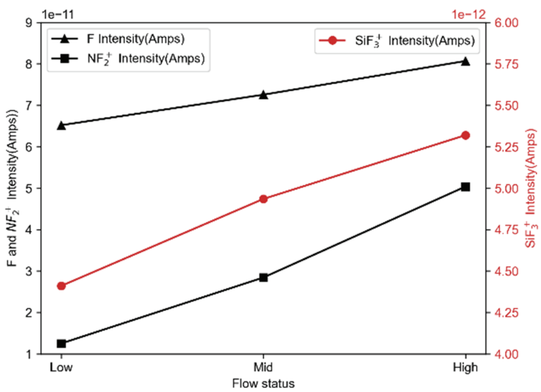
Table 6. Selection of QMS Peaks for Experiment

RGA	NF_3
Species/ Atomic Mass Unit	F/19
	NF_2/52
	SiF_3^+/85
	O_2/32
	$N_2$28

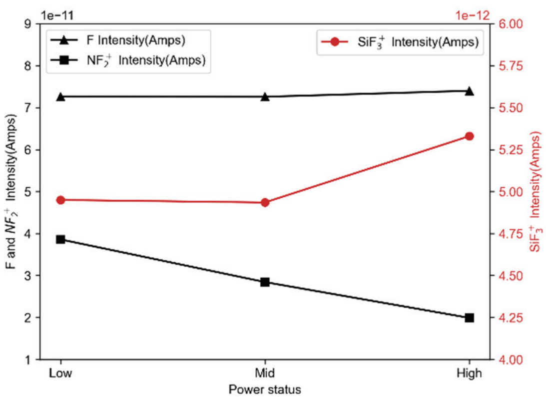
F is a by-product that can be produced from SiF_4 and NF_3 and can affect the cleaning rate and by-product formation. F radicals react with the by-product SiO_2 in the chamber and are emitted in the form of SiF_4 and O_2. Additionally, F radicals that do not participate in the cleaning reaction can exist in various forms such as F_2, SiF_4, and NF_3 upon emission, which are directly related to environmental issues associated with exhaust gases.

Fig. 13 shows the changes in by-products according to variations in Flow and Power. QMS analysis results show that as the flow rate increases, the QMS values of the main by-products increase significantly. The increase in SiF_3^+ with the increase in flow rate shows a similar trend to the increase in the cleaning rate. Additionally, the increase in NF_2^+ indicates an increase in the unreacted NF_3 that does not participate in the reaction. The increase in the intensity of F radicals can contribute to improving the cleaning rate, but the environmental impact must also be considered. Ultimately, while an increase in flow rate can enhance the cleaning rate, it indicates that the escalation of NF_3 emissions could accelerate the greenhouse effect.

The decrease in the intensity of NF_2^+ with the increase in RPS power indicates that higher power increases the dissociation rate of NF_3, reducing the NF_3 that does not participate in the cleaning process. The intensity of F shows no difference when power changes from Low Level to Mid Level but a slight increase when changed to High Level. In fact, there is no significant change in the cleaning rate when increasing from Low to Mid Level, but there is a 6% increase in cleaning rate when compared to the High Level.



(a)



(b)

Fig. 13. According to (a) flow and (b) power variations NF_3 cleaning by-product Ion-current intensity with QMS.

4. Conclusion

In this study, we quantitatively analyzed the effects of process variables on the cleaning rate and cleaning Stdev of an NF_3-based cleaning process in a 12-inch PECVD chamber.

In previous studies using multiple linear regression analysis, Power and Pressure had P-values of 0.42 and 0.68, respectively, indicating that their effects on the cleaning rate were not significant. In contrast, our study found that Power, Pressure, and Flow all had P-values close to 0, indicating statistical significance. Compared to previous studies, Power and Pressure had 3 times and 7 times greater effects on the cleaning rate, respectively. Furthermore, in our study's multiple linear regression analysis of cleaning Stdev, all three variables had significant values. The analysis of cleaning rate and cleaning Stdev showed a trade-off relationship between increasing the rate and reducing the standard deviation through the weights of process variables.

We also analyzed the by-products generated during the cleaning process based on QMS data. As the flow rate increased, the cleaning rate also increased, but the emission of gas, which contributes to the greenhouse effect, also increased. These results suggest that a balance must be struck between cleaning efficiency and environmental impact in semiconductor manufacturing processes.

Currently, extensive research is being conducted on chamber cleaning, including methods using a mixture of NF_3 and other gases and alternative cleaning gases such as COF_2 and F_3NO. This study highlights the need to consider the differences between research equipment and actual industrial equipment and provides a benchmark for the effectiveness of cleaning processes in current actual industrial environment. This study is expected to be useful when verifying the substitutability of alternative gases.

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