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Silicon Oxide Etching Process of NF_3 and F_3NO Plasmas with a Residual Gas Analyzer

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Abstract: The use of NF_3 is significantly increasing every year. However, NF_3 is a greenhouse gas with a very high global warming potential. Therefore, the development of a material to replace NF_3 is required. F_3NO is considered a potential replacement to NF_3. In this study, the characteristics and cleaning performance of the F_3NO plasma to replace the greenhouse gas NF_3 were examined. Etching of SiO_2 thin films was performed, the DC offset of the plasma of both gases (i.e., NF_3 and F_3NO) was analyzed, and a residual gas analysis was performed. Based on the analysis results, the characteristics of the F_3NO plasma were studied, and the SiO_2 etch rates of the NF_3 and F_3NO plasmas were compared. The results show that the etch rates of the two gases have a difference of 95% on average, and therefore, the cleaning performance of the F_3NO plasma was demonstrated, and the potential benefit of replacing NF_3 with F_3NO was confirmed.

Keywords: nitrogen oxide trifluoride; nitrogen fluoride oxide; reactive ion etch; silicon oxide etch

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1. Introduction

Since the 1980s, the use of NF_3 plasmas in semiconductor, display, and solar cell processing applications has been investigated [1]. NF_3 plasma is used to etch various thin films under reactive ion etching (RIE) conditions [2,3] or to clean a plasma-enhanced chemical vapor deposition (PECVD) chamber [4,5]. Cleaning the PECVD chamber is performed by supplying ions and radicals for cleaning through a remote plasma source (RPS) [6] or by directly supplying ions and radicals through an in situ plasma discharge [7]. In addition, NF_3 is attracting attention as a new etching technology, such as cryogenic electron beam induced etching (EBIE) [8,9] and highly selective etching [10]. NF_3 has a high etch rate, etching efficiency, and a relatively high chemical stability [2,11]. Accordingly, the use of NF_3 is significantly increasing every year. However, NF_3 is a greenhouse gas with a very high global warming potential of 16,100 and a lifespan of 500 years [12]. The contribution of NF_3 to the radiative forcing in the Earth's atmosphere is very small, ~0.01%, in 2011, but the use of NF_3 is increasing every day; therefore, this number continues to increase [13]. The share of NF_3 in fluorinated gases increased from 13–28% in 2005 to 17–36% in 2010, and NF_3 is currently the most widely used and released fluorinated gas [1,14]. Thus, it was included in the second commitment period of the Kyoto Protocol as the seventh greenhouse gas whose emissions are to be regulated [15].

Studies have been conducted to replace NF_3 [16,17]. Among them, F_3NO was considered a candidate gas to replace NF_3 [18]. Similar to NF_3, F_3NO does not contain perfluorocarbons. In addition, because its molecule has an N=O bond, its atmospheric life

is relatively short, and thus, its contribution to global warming is expected to be less than that of NF_3. The etch rate of F_3NO is almost the same as that of NF_3. However, further studies on F_3NO have not been conducted, and information on the mechanism occurring in the F_3NO plasma during the cleaning process is insufficient. Therefore, research on the F_3NO plasma to replace NF_3 is urgently needed.

The present study focused on evaluating and analyzing the properties of F_3NO plasma. Accordingly, the cleaning abilities of NF_3 and F_3NO were compared, and the characteristics of the F_3NO plasma were analyzed. The cleaning ability of the F_3NO plasma was evaluated by etching a SiO_2 film previously deposited on a Si wafer sample. Although the etching time of the small sample and the cleaning time of the PECVD chamber may not coincide, it was considered suitable for the evaluation of the cleaning ability of the gas. To analyze the etch mechanism, the etching plasma was diagnosed using a residual gas analyzer (RGA) and a high-voltage probe. The reactions in the F_3NO plasma were predicted by comparing the types and intensity of ions generated in the NF_3 and F_3NO plasmas. In addition, the etch rates of the SiO_2 thin film using the NF_3 and F_3NO plasmas were compared to confirm whether the F_3NO plasma can replace NF_3.

2. Materials and Methods

The plasma etching equipment used in this study is shown in Figure 1. We manufactured the RIE equipment with a direct capacitively coupled plasma chamber to measure the plasma etching characteristics. The detailed geometry of the device has been shown in a previous study [19]. A coolant path was formed in the electrode, which was designed to maintain a constant temperature (15 °C) during the process.

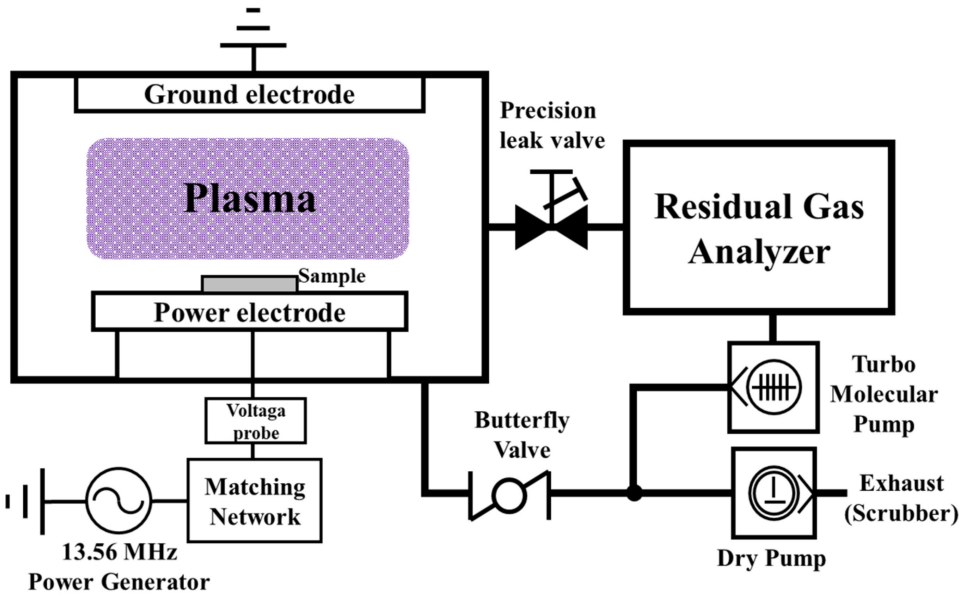

Figure 1. Plasma etching equipment setup.

The sample used for etching was a SiO_2 thin film deposited on a Si wafer. The size of the sample was 30 mm × 30 mm, and the thickness of the thin film was 2 μm. NF_3 and F_3NO were used as process gases for etching. The F_3NO used in the experiments was manufactured and supplied by SK Materials (Sejong, Korea) and the National NanoFab Center (Daejeon, Korea). The purity of the provided F_3NO gas was 99.995%. The injected process gas was controlled using mass flow controllers. The process flow rate was fixed at 120 sccm. After the injection of the process gas, the process pressure was adjusted using a butterfly valve. The working pressure range was 130–270 mTorr. This working pressure range was set to confirm the possibility of cleaning in situ with a small amount of gas in the chamber while reducing the amount of cleaning gas without any additional high

flow MFC configuration. After reaching the process pressure, the discharge power was applied through the RF power generator. The RF input power range was 240–400 W, and the process time was fixed at 3 min.

Mass spectrometry measurements were performed using an RGA (RGA 300, SRS, Sunnyvale, CA, USA). As shown in Figure 1, the RGA is equipped with a differential pump system. The pressure of the differential pump system was fixed at 0.8 mTorr regardless of the process pressure. At this time, the ionization energy of the RGA was fixed at 70 eV. The DC self-bias (DC offset) was measured using a high-voltage probe to determine the characteristics of the NF_3 and F_3NO plasmas. The etching rate of the thin film was evaluated after etching by measuring its thickness using the spectroscopic reflectometry method via the S-TRC series (Wonwoo Systems Co., Ltd., Seoul, Korea) [20].

3. Results and Discussion

To compare the characteristics of the NF_3 and F_3NO plasmas and to understand the characteristics of the latter, a DC offset measurement during the RIE plasma discharge was performed (Figure 2). The F_3NO plasma showed a similar DC offset value very close to that of the NF_3 plasma.

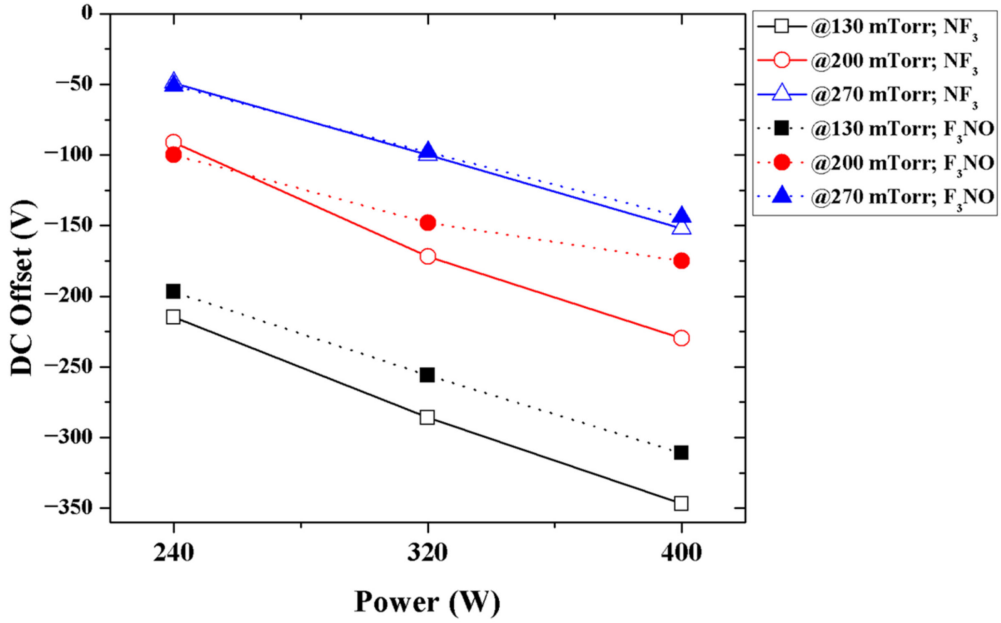

Figure 2. DC offset of the RF electrode during plasma discharge at a total flow rate of 120 sccm.

The NF_3 plasma has a very high electronegativity [21,22]. Therefore, when compared with fluorocarbon plasmas, the NF_3 plasma shows a relatively low DC offset value. Plasma with a high electronegativity tends to be unstable and easily collapses. In this case, the NF_3 plasma is discharged only in a part of the chamber, and the plasma collapses in other parts; therefore, these parts may not be exposed to the plasma. Alternatively, a constant discharge may not occur but may flicker and cause discharge.

The comparison results of the DC offset of the NF_3 and F_3NO plasmas show that the electronegativity of the F_3NO plasma can also be quite considerable. In the case of the NF_3 plasma, an inert gas (e.g., He, Ar) was diluted and discharged to increase the stability and uniformity of the plasma and enhance etch rates [23–26]. Inert gases rarely participate in chemical reactions in the plasma but can have a great influence on the discharge process. The DC offset result indicates that the characteristics of the F_3NO plasma can also be comparable to those of the NF_3 plasma. Thus, in future studies, dilution with an inert gas, such as Ar, is recommended.

Figure 3 shows the current of F+ ions and etch products (SiF, SiF_2, and SiF_3) generated from the NF_3 and F_3NO plasmas when etching SiO_2 thin films. As the pressure and power

increased, the intensity of the peak of F ions and the etch product also increased. At this time, when the pressure or discharge power was low, more F ions were generated in the F_3NO plasma than in the NF_3 plasma. In addition, the lower the discharge power, the higher the generation of etch products in F_3NO than in NF_3. These findings confirmed that the etching of F_3NO occurs more actively at low power and pressure. In addition, as the power increases, the intensity of F ions in NF_3 rapidly increases, whereas in the F_3NO plasma, the F ions gradually increase even if the discharge power of F increases. As will be shown further, this trend is similar for other ions as well. Consequently, the plasma density of F_3NO reacts more slowly to the change of the discharge power compared to NF_3.

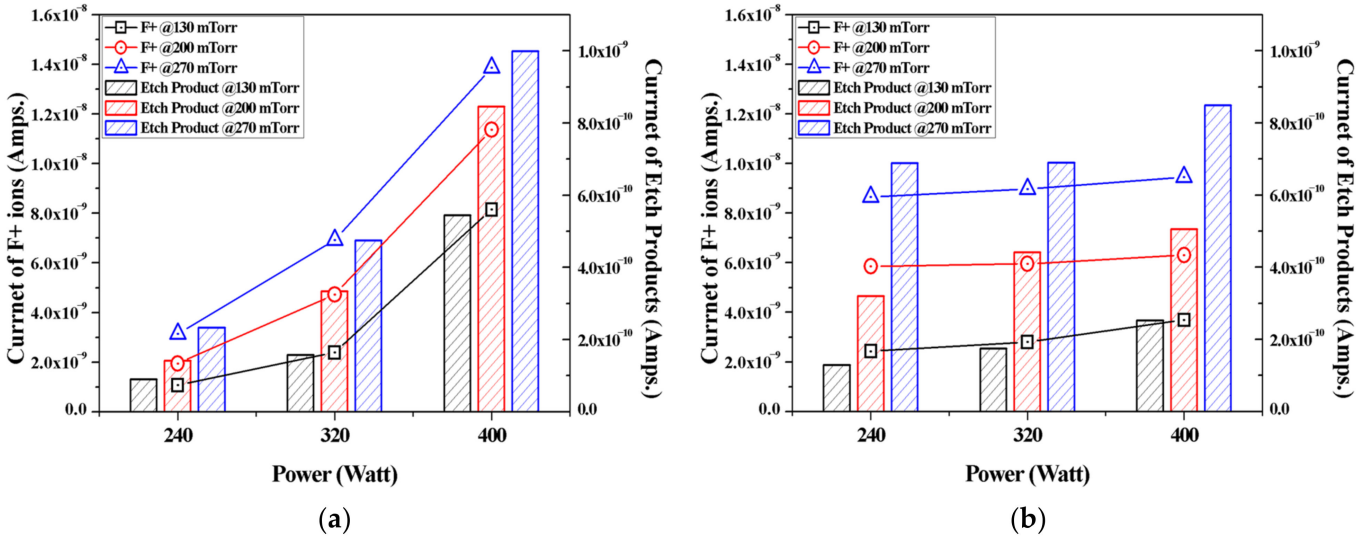

Figure 3. (**a**) Intensity of F+ ions and the sum of the etch product ions (SiF+, SiF_2+, and SiF_3+) during NF_3 plasma silicon oxide etching as functions of the input power for various working pressures; (**b**) Intensity of F+ ions and the sum of the etch product ions (SiF+, SiF_2+, and SiF_3+) during F_3NO plasma silicon oxide etching as functions of the input power for various working pressures.

Among the ions generated in the NF_3 and F_3NO plasmas during the silicon oxide thin film etching, O and O_2 were more common in the F_3NO plasma under all conditions (Figure 4). Compared with the F_3NO plasma, O and O_2 ions hardly occurred in the NF_3 plasma. In the case of the F_3NO plasma, O and O_2 ions were simultaneously generated by O contained in F_3NO and O_2 gas already present in the chamber, whereas the NF_3 plasma generated O and O_2 ions only from O_2 gas existing in the base. Therefore, when the pressure increased, the intensity of O and O_2 ions generated in the NF_3 plasma was almost unchanged, whereas in the F_3NO plasma, when the pressure increased, O and O_2 ions appeared to rapidly increase compared to the NF_3 plasma.

Figure 5 shows the peak intensities of the major ions generated in the NF_3 and F_3NO plasmas during the etching of a silicon oxide thin film. N, N_2, and F_2 ions occurred more in F_3NO at low discharging powers and more in NF_3 at higher discharging powers. Conversely, NF_2 ions occurred more in the NF_3 plasma under all conditions.

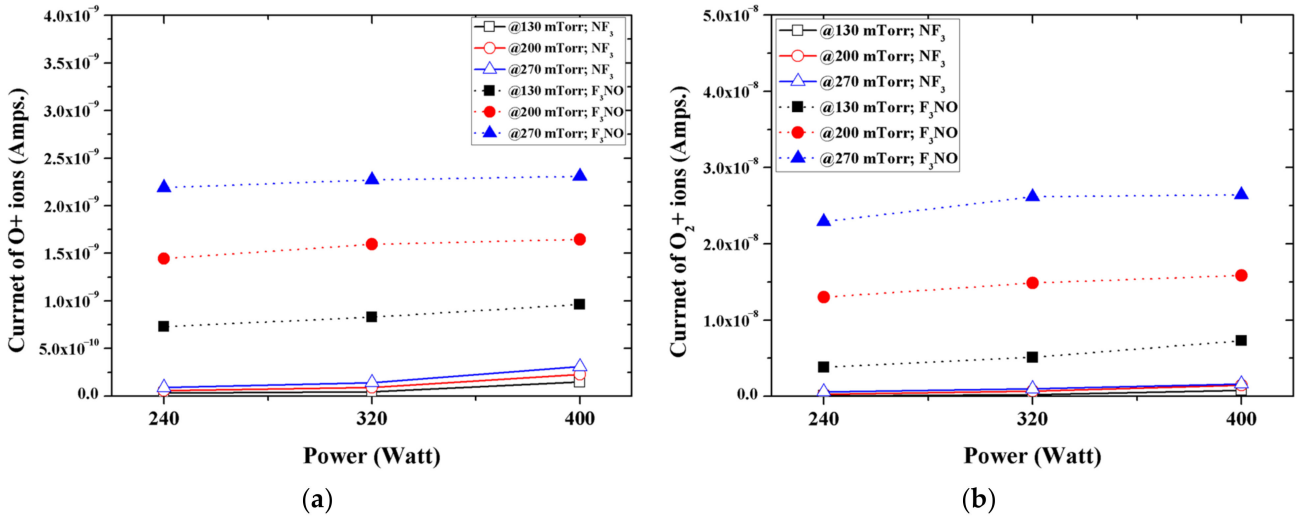

Figure 4. Intensity of: (**a**) O+ ions; (**b**) O_2+ during plasma silicon oxide etching as functions of input power for various working pressures.

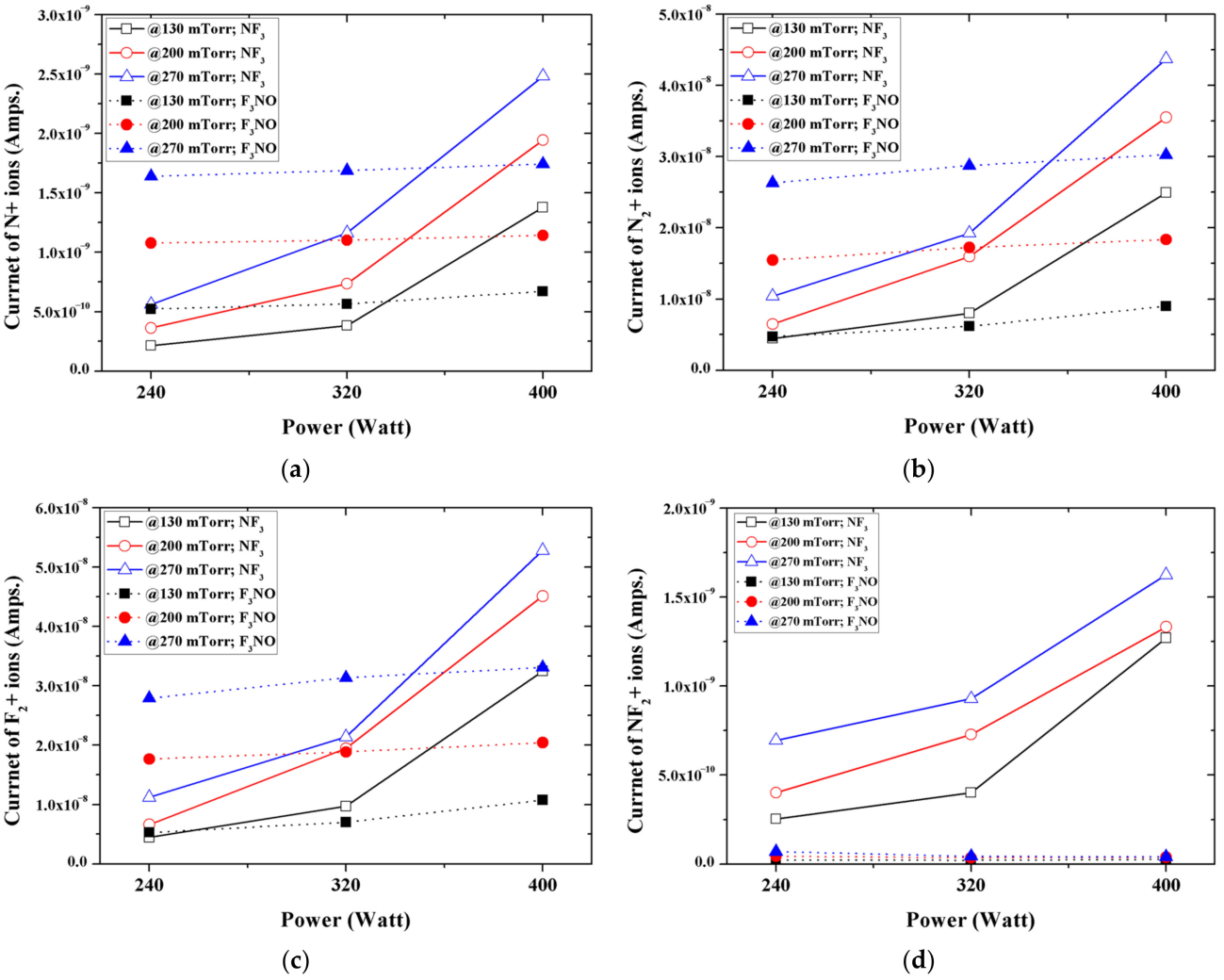

Figure 5. Intensity of: (**a**) N+ ions; (**b**) N_2+ ions; (**c**) F_2+ ions; (**d**) NF_2+ ions during plasma silicon oxide etching as functions of the input power for various working pressures.

Figure 6 shows the intensity of NO and NO_2 ions generated in the NF_3 and F_3NO plasmas during the etching of silicon oxide thin films. When the discharge power was low, the NO ions generated in the F_3NO plasma were more than those of the NF_3 plasma (numerical value). However, as the discharge power increased, the number of NO ions in the F_3NO plasma gradually decreased, whereas those in the NF_3 plasma rapidly increased and became almost the same as the peak intensity of NO ions generated in the F_3NO plasma. Conversely, many more NO_2 ions occurred in the F_3NO plasma under all conditions.

$$\text{In the } NF_3 \text{ and } F_3NO \text{ plasmas, NO was produced through the following reaction : } N_2\left(A^3\Sigma_u^+\right) O \rightarrow NO + N. \quad (1)$$

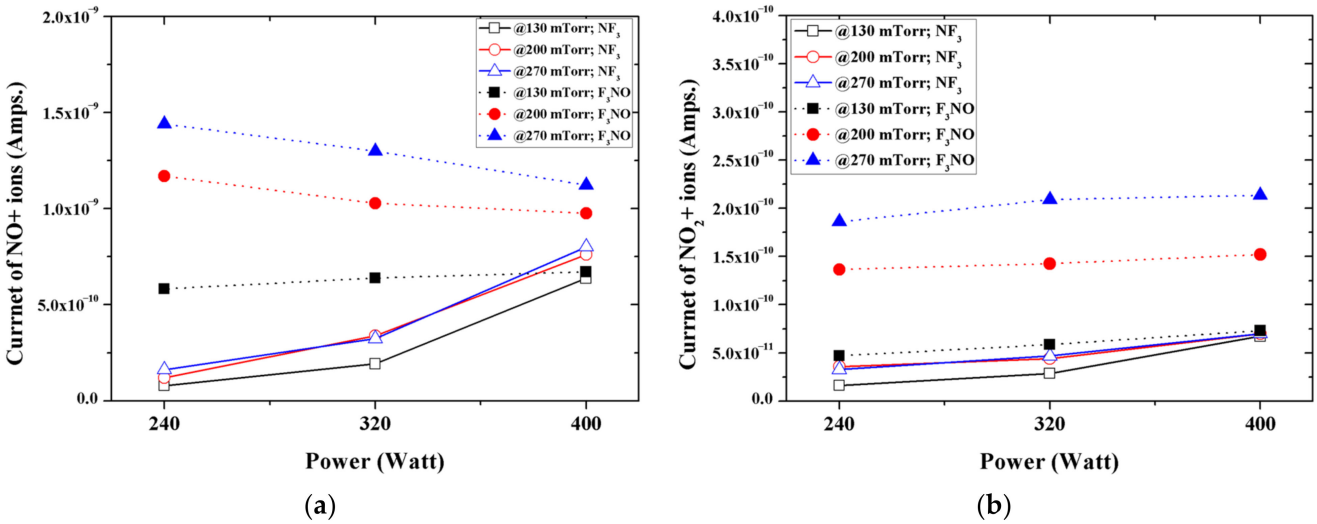

Figure 6. Intensity: of (**a**) NO+ ions; (**b**) NO_2+ ions during plasma silicon oxide etching as functions of the input power for various working pressures.

Metastable N_2 is produced mostly by collisions with a high-energy electron, making the mechanism more significant in an electronegative gas discharge, such as NF_3 and F_3NO. At a higher discharge power, higher energy electrons are supplied, thus increasing the density of NO ions [27]:

$$N + O_2 \rightarrow NO + O. \quad (2)$$

A reaction involving atomic nitrogen that resulted in a different density of NO ions in the F_3NO plasma and the NF_3 plasma was more important in an oxygen-rich plasma [28,29]. As shown in Figure 4a, because F_3NO is an oxygen-rich plasma, reaction (2) became significant, and a large amount of NO ions were produced.

In the F_3NO plasma, NF is decomposed through the following reaction.

$$NF_2 + O \rightarrow F + FNO. \quad (3)$$

The species produced in the primary reactions led to secondary reactions which formed NO_2 ions through the following exothermic reactions:

$$FNO + O \rightarrow F + NO_2, \quad (4)$$

$$FO + NO \rightarrow F + NO_2, \quad (5)$$

$$N_2O + NO \rightarrow N2 + NO_2, \quad (6)$$

$$NO + O_3 \rightarrow O_2 + NO_2. \quad (7)$$

In the case of the NF_3 plasma, the above reaction is not significant because the number of O ions is remarkably small, but F_3NO causes a more significant reaction. Therefore, the number of NF_2 and NF ions are fewer in the F_3NO plasma than in the NF_3 plasma, whereas ions such as N, N_2, and F are present in similar amounts in the F_3NO plasma and the NF_3 plasma.

In the NF_3 plasma, NO ions may be generated through the bonding of O and N ions, which are etching by-products, or through a process in which N ions form Si–O–N bonding on the surface of the silicon oxide thin film [30]. In the F_3NO plasma, NO is formed by the N and O ions contained in F_3NO. In the case of F_3NO, this condition becomes the main mechanism. NO formed in this way forms NO_2 through the following reaction:

$$NO + O + M \rightarrow NO_2 + M. \quad (8)$$

In the NF_3 plasma, because the number of O ions was remarkably small, this oxidation reaction occurred only to a small extent. Conversely, in the F_3NO plasma, as the number of O ions was much larger, the extent of the oxidation reaction was more significant. When the discharge power was increased, the number of NO formed was almost unchanged, but the peak of NO ions decreased due to the considerable oxidation of NO.

Figure 7 shows the SiO_2 etch rate according to the discharge power and process pressure. The results imply that the lower the pressure and discharge power, the higher the etch rate of F_3NO. This is because when the pressure and discharge power is low, chemical etching occurs more easily because the number of F ions generated is greater in F_3NO. Conversely, the DC offset at a low power has a small absolute value for the NF_3 and F_3NO plasmas; therefore, the ion bombardment energy does not have a significant effect on etching. When the discharge power was increased, the DC offset value of the NF_3 plasma became larger than that of the F_3NO plasma, so the etch rate of NF_3 also became higher. When the discharge pressure and discharge power increased, the intensity of F ions also increased as NF_3 increased, so the etch rate decreased in F_3NO. Furthermore, the etch rate of silicon oxide during F_3NO plasma etching was approximately 95.0% of the rate during NF_3 plasma etching.

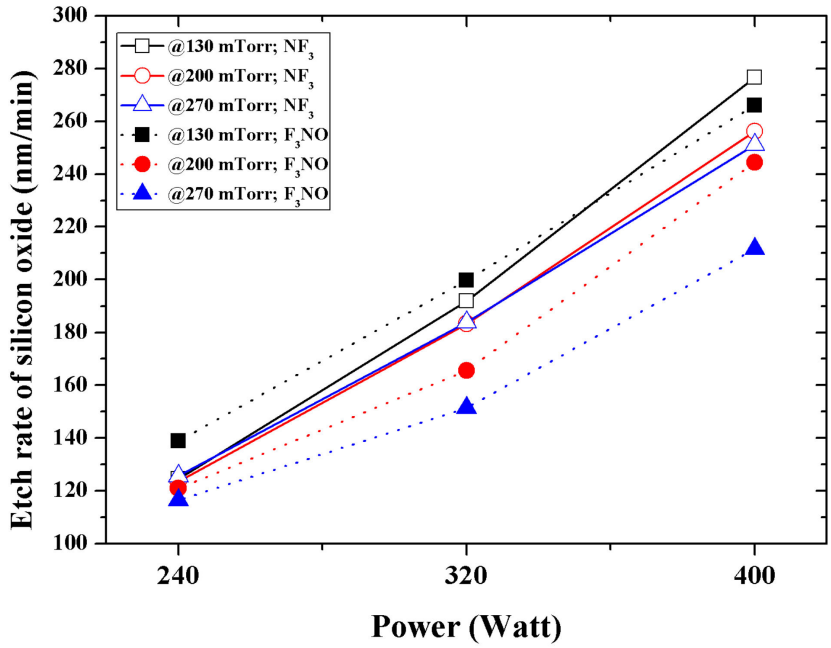

Figure 7. Etch rate as a function of input for various working pressures during plasma silicon oxide etching at a total flow rate of 120 sccm.

We performed SEM measurements to determine whether O or N ions present in the plasma had a negative effect on the etching quality. Figure 8 shows a SiO_2 surface of SEM images after the etching process at 400 W discharge power and 270 mTorr pressure. For accurate SEM measurements, a platinum coating was applied on the surface by sputtering. The round shape particles in the figures are platinum nanoparticles from the platinum coating. The size of these nanoparticles is in order of several nanometers. Besides platinum nanoparticles, no other structures such as cracks or holes were found on the surface. No significant difference was observed between the SEM images of the unprocessed and processed surface of SiO_2. Therefore, it was confirmed that O or N ions in F_3NO did not have a negative effect on the etching quality.

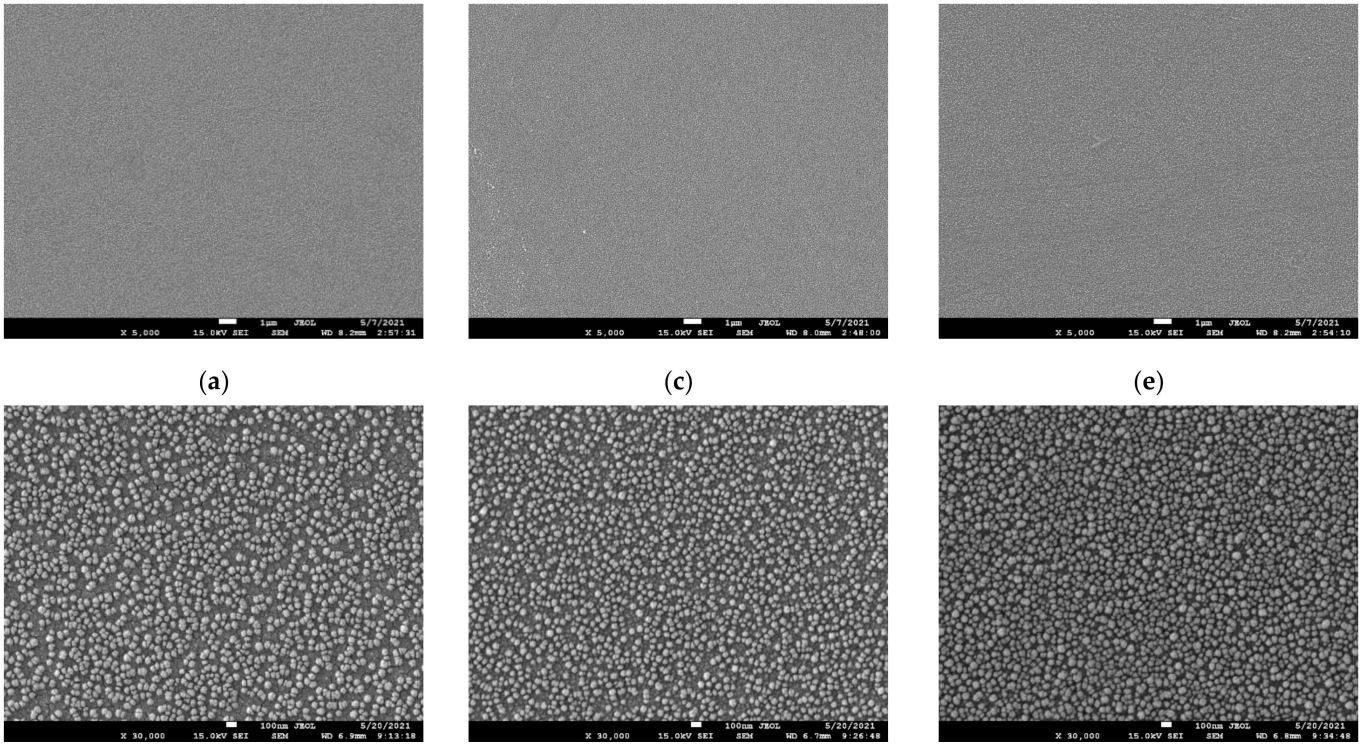

Figure 8. Surface of the SEM images of the SiO_2 samples: without etching of (**a**) ×5000, (**b**) ×30,000, at 400 W discharge power and 270 mTorr process pressure with NF_3 plasma of (**c**) ×5000, (**d**) ×30,000 and F_3NO plasma of (**e**) ×5000 and (**f**) ×30,000.

Figure 9 shows EDS spectra of the SiO_2 surface without process and after etching at a 400 W discharge power and 270 mTorr pressure with the NF_3 and F_3NO plasmas. The C peak in the EDS spectra was caused either by carbon contamination or by the window in the detector. Except for carbon and platinum (from the platinum coating), no peaks other than O and Si were found in the EDS spectra. This indicates that nitrogen, oxygen, or NO did not chemically contaminate the SiO_2 surface during the etching process.

The mass ratio of silicon and oxygen is noticeable in the EDS spectra. The mass ratio of silicon and oxygen on the SiO_2 surface is almost the same when the process is not performed and when the NF_3 etching process is performed. However, the mass ratio of O appears less on the SiO_2 surface after F_3NO etching. This may be caused by the following reaction on the SiO_2 surface during F_3NO etching.

$$O(s) + NO(g) \rightarrow NO_2(g). \quad (9)$$

As above, NO ions absorb O in the SiO_2 surface to decrease surface oxidation [31]. Therefore, the F_3NO etched SiO_2 surface has a smaller oxygen mass ratio than the NF_3 etched SiO_2 surface. Moreover, this de-oxidation process increases the Si etching rate, especially during etching with F_3NO at low pressure and low power with a significant quantity of NO ions.

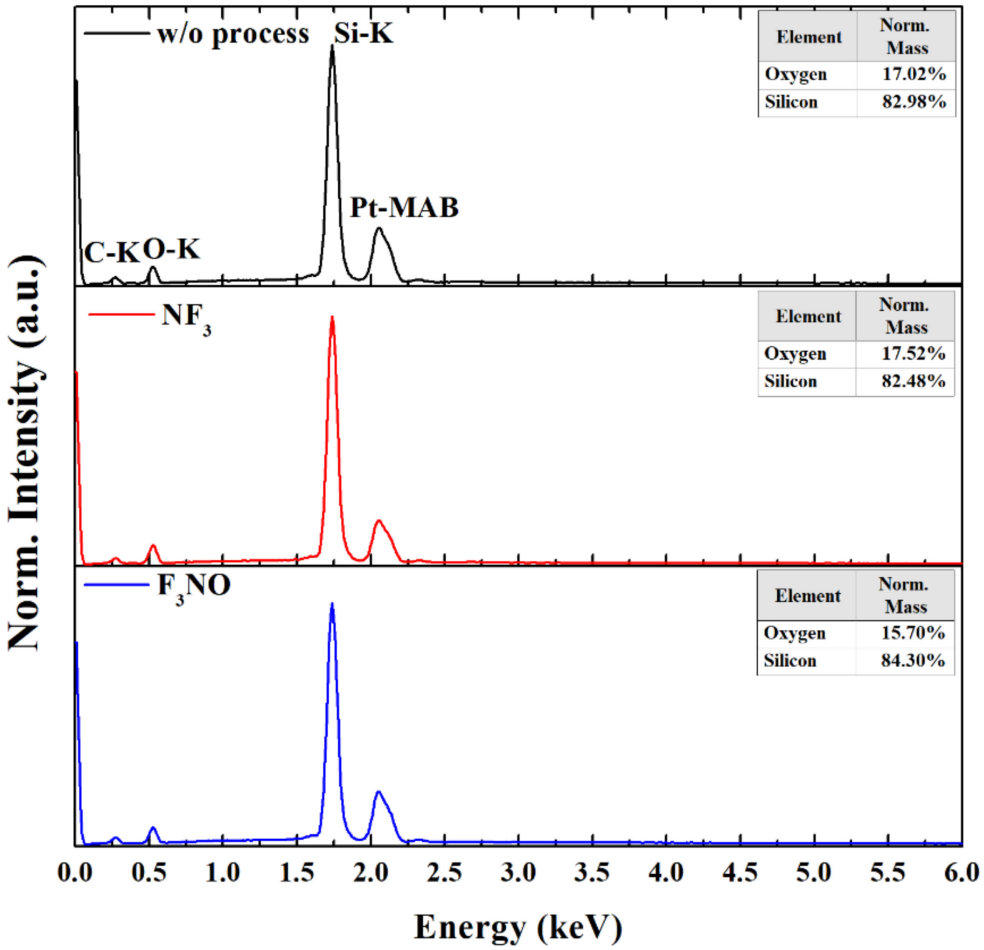

Figure 9. EDS spectra of the SiO_2 surface without etching, at 400 W discharge power and 270 mTorr process pressure with NF_3 plasma and F_3NO plasma.

4. Conclusions

The DC offset was measured during NF_3 and F_3NO plasma discharges. Compared with the DC offset of the NF_3 plasma, the F_3NO plasma showed an almost similar DC offset value. This finding confirms that the F_3NO plasma, similar to the NF_3 plasma, can have a very high electronegativity. Moreover, the NF_3 plasma, similar to the F_3NO plasma, may also exhibit unstable or non-uniform characteristics. Therefore, the diluent of an inert gas into the F_3NO plasma can be effective.

The ions generated in the NF_3 plasma and the F_3NO plasma during the etching of the SiO_2 thin film were measured through the RGA. In the case of F ions, when the discharge power and discharge pressure were low, more F_3NO plasmas were generated than NF_3 plasmas. The result was the same for the etching by-products (SiF, SiF_2, and SiF_3). In addition, as the power increased, the intensity of F ions in NF_3 rapidly increased, whereas in the F_3NO plasma, the ions of F gradually increased even if the discharge power of F increased. This result showed a similar trend for other ions afterward, implying that the plasma density of F_3NO reacts more slowly to the change of the discharge power compared to NF_3. Ions O and O_2 generated during the plasma discharge were much more significant in the F_3NO plasma than in the NF_3 plasma, which is attributed to the O ions contained in

F_3NO. Furthermore, the intensity of O ions can affect the etching mechanism of the F_3NO plasma. F_2, N, N_2 ions occur more in F_3NO at a low discharge power and occur more in NF_3 at a high discharge power. In contrast, NF_2 ions are much higher in NF_3 ions under all conditions. O ions in F_3NO cause a reaction to decompose NF_2. When the discharge power is low, the NO ions of F_3NO are generated in higher amounts compared to the NF_3 plasma. However, as the discharge power increases, the number of NO ions in F_3NO gradually decreases, whereas the NO ions in the NF_3 plasma rapidly increase, and the intensity of the peak of NO generated in F_3NO becomes almost similar. Conversely, NO_2 ions occur more in the F_3NO plasma under all conditions. In the F_3NO plasma, many NO ions are generated in the process of decomposing NF_2. However, when the pressure increases, NO ions are oxidized by O ions to form NO_2 ions, and thus the number of NO ions decreases. Through this oxidation reaction, many more NO_2 ions are generated in the F_3NO plasma than in the NF_3 plasma.

The SiO_2 etch rates of the NF_3 and F_3NO plasmas were compared. The results show that the lower the pressure and discharge power, the higher the etch rate of F_3NO. This is because the intensity of F ions is higher in the F_3NO plasma at low pressure. As the discharge power increases, the intensity of F ions in the NF_3 plasma increases. Therefore, the etch rate of the NF_3 plasma increases. The etch rate of silicon oxide during F_3NO plasma etching was approximately 95.0% of the NF_3 plasma etching rate.

To compare the etch qualities, SEM measurements were performed. There was no difference between the unetched and etched SiO_2 surface with the NF_3 and F_3NO plasmas. Therefore, we found that N or O ions in F_3NO did not negatively affect the etch quality. The results of this study confirm the cleaning properties of F_3NO. Nonetheless, the limitation of this study is that only NF_3 and F_3NO plasmas were compared. In addition, EDS measurements were performed in parallel to assess the possibility of chemical contamination of the surface by ions in F3NO and phenomena occurring on the SiO_2 surface during etching. As a result of the measurement, no chemical contamination was observed during etching with NF_3 plasma or F_3NO. Unlike NF_3 plasma etching, it was observed that the mass ratio of oxygen of the SiO_2 surface decreased during F_3NO plasma etching. This may be attributed to the de-oxidation process of the SiO_2 surface by NO ions.

The characteristics of the F_3NO plasma were identified through these results, and the potential for replacing F_3NO with NF_3 was confirmed. Further studies will be needed when inert gases, such as Ar or He, are used as diluent. In addition, higher pressures need to be evaluated for the cleaning ability.

Author Contributions: Conceptualization, M.-H.K., J.-H.K. (Jung-Hun Kwak) and G.-C.K.; methodology, W.-J.K., H.-T.K. and G.-W.S.; validation, H.-T.K. and J.-H.K. (Ji-Hwan Kim); formal analysis, W.-J.K., I.-Y.B. and G.-W.S.; investigation, I.-Y.B., J.-H.K. (Ji-Hwan Kim), Y.-S.P. and Y.C.; resources, M.-H.K., Y.C. and B.-H.K.; data curation, I.-Y.B and Y.-S.P.; writing—original draft preparation, W.-J.K.; writing—review and editing, W.-J.K.; supervision, G.-C.K. All authors have read and agreed to the published version of the manuscript.

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