

## Effects of N<sub>2</sub> addition on chemical etching of silicon nitride layers in F<sub>2</sub>/Ar/N<sub>2</sub> remote plasma processing

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### Abstract

In this study, chemical dry characteristics of silicon nitride layers were investigated in the F<sub>2</sub>/N<sub>2</sub>/Ar remote plasma. A toroidal-type remote plasma source was used for the generation of remote plasmas. The effects of additive N<sub>2</sub> gas on the etch rates of various silicon nitride layers deposited using different deposition techniques and precursors were investigated by varying the various process parameters, such as the F<sub>2</sub> flow rate, the addition N<sub>2</sub> flow rate and the substrate temperature. The etch rates of the various silicon nitride layers at the room temperature were initially increased and then decreased with the N<sub>2</sub> flow increased, which indicates an existence of the maximum etch rates. The etch rates of the silicon oxide layers were also significantly increased with the substrate temperature increased. In the present experiments the F<sub>2</sub> gas flow, addition N<sub>2</sub> flow rate and the substrate temperature were found to be the critical parameters in determining the etch rate of the silicon nitride layers

### 1. Introduction

Remote plasma cleaning processes of silicon dioxide and PE-nitride(silicon nitride deposited by PECVD) layers using perfluorocompounds(PFCs) such as C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, C<sub>4</sub>F<sub>8</sub>, and NF<sub>3</sub> have been studied and used in the industry [1-7]. Re-emitted PFCs during chamber cleaning are known to cause serious global warming effect in the atmosphere [1-5]. Various ways to reduce the emission of PFCs have been investigated in the semiconductor industry by the use of alternative process chemicals, process optimization and new abatement technologies including destruction and recovery [2]. Therefore, remote plasma cleaning process using less expensive alternative gases such as F<sub>2</sub> can be very effective in the cleaning of SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> thin films because F<sub>2</sub> gas can be generated on-site at lower price than NF<sub>3</sub>. But the problems of F<sub>2</sub> gas cleaning process are its high toxicity and reactivity [4]. Successful F<sub>2</sub> line passivation methods and F<sub>2</sub> handling measures have been developed for safety during the use of F<sub>2</sub> gas [5-6]. CVD chamber cleaning process using F<sub>2</sub> for silicon oxide and silicon nitride has been rarely reported. Therefore, development of remote F<sub>2</sub> plasma cleaning process of silicon nitride or oxide is needed.

### 2. Experiments

Fig.1 show a schematic diagram of the PECVD system used in the present experiment equipped with a toroidal-type remote plasma source (New Power Plasma Co.) with the power of 10kW and the AC frequency of 400kHz and the gas sampling system [3-7]. The silicon nitride PECVD chamber has a load-lock chamber and a pressure controller with a throttle valve. Before the cleaning experiments, in order to prevent the corrosion and explosive reaction of metal surfaces, fluorine passivation process of metal surfaces inside the gas lines of the remote plasma source, gas cabinet system, and F<sub>2</sub> deliver lines was performed by using a diluted F<sub>2</sub> gas flow [5-6]. For delivery of F<sub>2</sub> gas from the gas bottle to the remote plasma source, a double tubing system was adopted. In this experiment, a bottled F<sub>2</sub> with a purity of 98% was used.

### 3. Results and discussion

In order to see the effect of F<sub>2</sub> concentration in the input gas, the effect of N<sub>2</sub>/(F<sub>2</sub>+Ar) flow ratio on the cleaning rate was investigated. The cleaning rates as a function of the N<sub>2</sub>/(F<sub>2</sub>+Ar) gas flow ratio while keeping the total (F<sub>2</sub>+Ar) gas flow at 3000 sccm was shown in Fig. 2. Increasing the F<sub>2</sub>/(F<sub>2</sub>+Ar) gas flow ratio from 16.7% to 83.4% enhanced the cleaning rate from 113 to 185 nm/min. The cleaning rate was increased by a factor of 1.64 in this experiment.

Fig. 3 shows the cleaning rates of PE-nitride layers as a function of the cleaning temperature. Total gas flow was fixed at 3000sccm and the substrate temperature was varied from 25 to 350 °C. Cleaning rate of PE-nitride layers by 29% F<sub>2</sub> remote plasma was increased from considerably 57.5 to 5916 nm/min as the substrate temperature was varied from 25 to 350°C. The cleaning rate of PE-nitride layer was also increased as the F<sub>2</sub> concentration increases from 29% to 68% at the same cleaning temperature.

Fig. 4 shows the FT-IR spectra obtained under the conditions of F<sub>2</sub> gas flow with plasma-on state. The spectra in Fig. 4 were obtained at the exhaust line under the condition of working pressure of 2Torr, remote plasma source power of 1204 W and F<sub>2</sub> (500 sccm)/Ar(500 sccm) gas flow ratio. The FT-IR spectra during the remote F<sub>2</sub> plasma cleaning PE-nitride layer show the main emitted species of CF<sub>4</sub>, SiF<sub>4</sub>, HF, H<sub>2</sub>O and CO<sub>2</sub>. The new peaks of SiF<sub>4</sub> and CF<sub>4</sub> are observed

during the cleaning of silicon nitride layer.

#### 4. Summary

We have successfully carried out gas line passivation using diluted F<sub>2</sub> gas before cleaning experiments. It was found that F<sub>2</sub> remote plasma generated by a toroidal-type remote plasma source is very effective in obtaining the high cleaning rate of PE-nitride layers. Cleaning rates of PE-nitride layers were increased with increasing the F<sub>2</sub> flow rate and F<sub>2</sub>/(F<sub>2</sub>+Ar) flow ratio. The cleaning rate of PE-nitride layers was also considerably increased as cleaning temperature varies 25 to 350°C. Monitoring of emitted gases during remote plasma cleaning on the condition of F<sub>2</sub> (500sccm)/Ar(500sccm) shows the main cleaning reaction products of CF<sub>4</sub>, F<sub>2</sub>, and SiF<sub>4</sub>.

#### References

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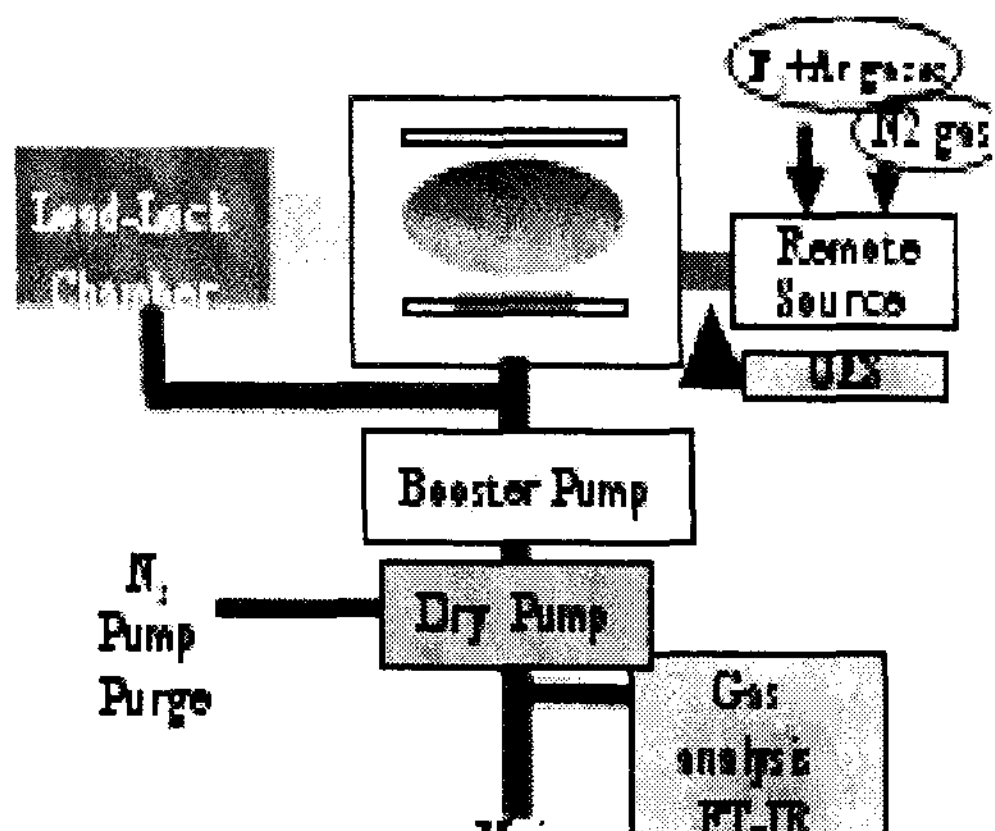


Fig.1. Schematic of the PECVD system equipped with the remote plasma source used for F<sub>2</sub> chamber cleaning.

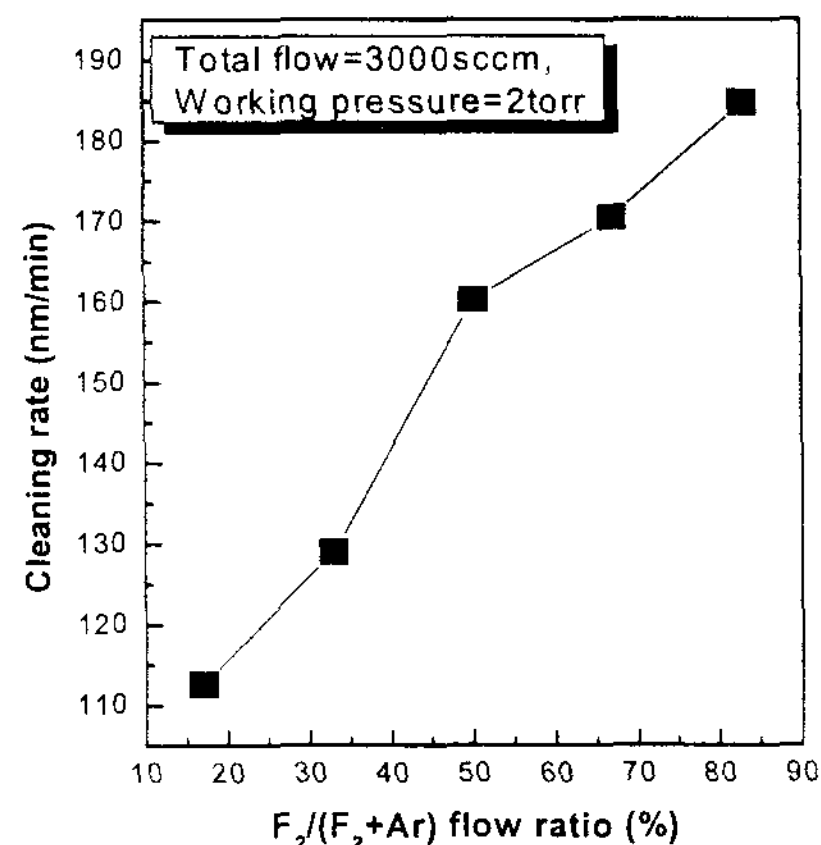


Fig.2. Cleaning rate of the PE-nitride layer as a function of F<sub>2</sub>/(F<sub>2</sub>+Ar) flow rate.

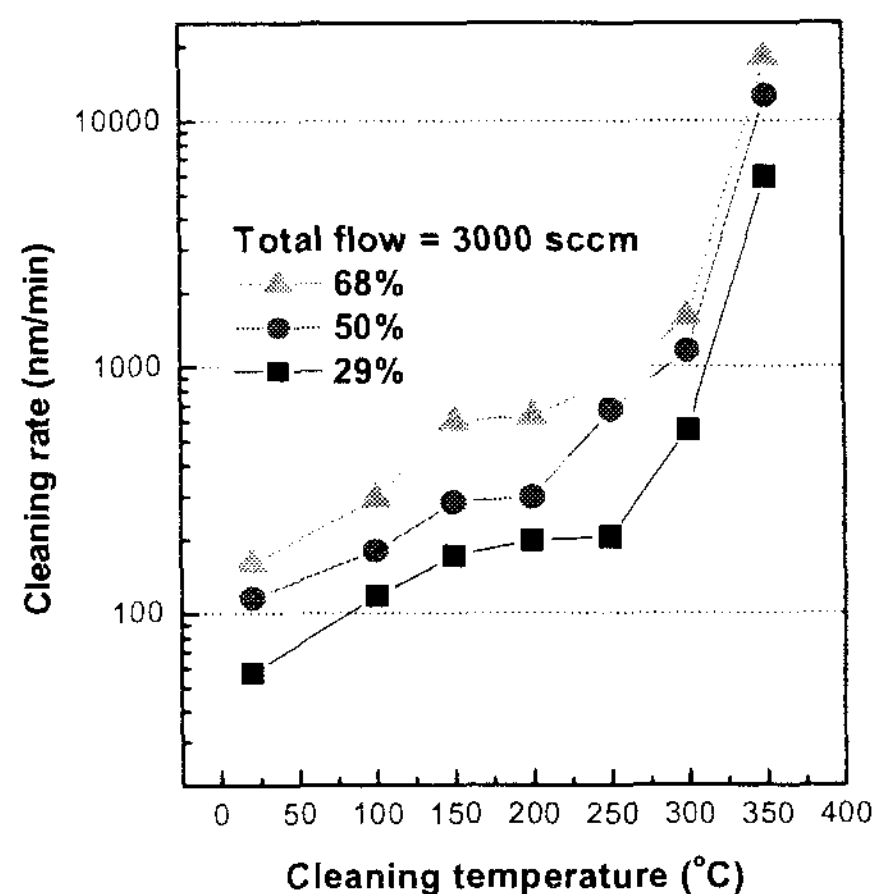


Fig.3. Cleaning rate of the silicon nitride layer as a function of cleaning temperature.

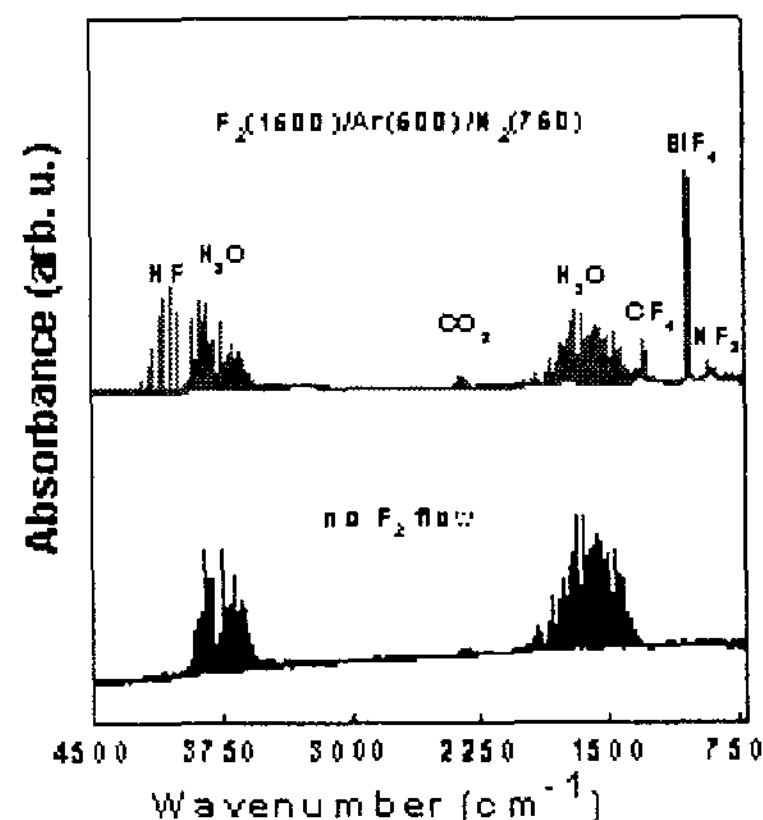


Fig.4. FT-IR spectra from the gas exhaust line with no F<sub>2</sub>(plasma-off), F<sub>2</sub>(1500sccm)/Ar(500sccm)/N<sub>2</sub>(750sccm) plasma.