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Adsorption Behavior of Various Fluorocarbon Gases on the Silicon Wafer Surface

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1. Introduction

The improvement of ULSI performance is required to make device structure miniaturize. The microfabrication in the etching process is one of the indispensable technologies for miniaturization of the device structure. Therefore, the etching technology of high aspect ratio is required. Reactive ion etching (RIE) process is required to inhibit the micro loading effect and to make the selectivity between SiO_2 and photo-resist as high as possible. Up to now, many researchers have been studying about these subjects [1,2]. In RIE process, the etching reaction is promoted by assist of the high-energy ion irradiated to etching gases which are adsorbed to the substrate surface [3,4]. Therefore, one of the factors that determine the etching characteristic is the adsorption behavior of etching gas to the substrate surface. In order to realize the etching technology of high aspect ratio, the etching gas that has high adsorption capability (high selectivity) to the SiO_2 surface is required. Thus, it becomes important to clarify the adsorption behavior of etching gas to the substrate surface. The purpose of this paper is to clarify the adsorption behavior (surface selectivity) of etching gases to the various substrate surfaces.

2. Experiment

Fig. 1 shows the molecular structure and the binding energy of used fluorocarbon gases. (a) C_4F_8, (b) cyclic C_5F_8 and (c) advanced C_5F_8 were evaluated as fluorocarbon etching gases (C_xF_y gases). Fig. 2 shows the schematic diagram of experimental setup. Atmospheric pressure ionization mass spectrometer (APIMS) was used as measuring equipment. The adsorption behavior of C_xF_y gases was examined by measuring the adsorption amount to various surfaces. SiO_2, Si, and photo-resist were prepared on the inner surface of the electro polished stainless-steel tube and used as test surfaces instead of silicon wafer surface. The adsorption behavior to the wafer surface can be artificially examined by using theses sample tubes. The measurement procedure of the adsorption amount is as follows. At first, the sample tube was installed in the predetermined position of an experimental setup shown in a fig. 2. Then, the sample tube was maintained at predetermined temperature (25, 60, 100, 150 and 200 degrees C). And argon (Ar) gas contained 100ppb of C_xF_y gas was introduced to the sample tube. The experiment was carried out using ultra-high purity Ar gas as a carrier gas. The impurity concentration in Ar gas was below 0.2 ppb. As C_xF_y gas was adsorbed on the inner surface of sample tube to some extent, we measured detected time for each C_xF_y gas by API-MS.

3. Results and Discussion

Fig. 3 shows the adsorption behavior model of C_xF_y gases introduced to the various sample tubes. The total number (Q_T) of adsorbed molecules on the inner surface of the sample tube can be obtained from the formula shown as follows;

$$Q_T = \text{Concentration} \times \text{Flow Rate} \times \text{Detection Time}$$

Fig. 4 shows the adsorption behavior of various C_xF_y gases on the SiO_2 surface at 25 degrees C. The vertical axis shows concentration of C_xF_y gas and horizontal axis shows detection time. Advanced C_5F_8 took the longest time to be detected. It was found that the easiest to adsorb gas on the SiO_2 surface is advanced C_5F_8. The ratio of the adsorption amount of various C_xF_y gases was as follows;

C_4F_8: cyclic C_5F_8: advanced C_5F_8 = 1: 31: 96.

Fig. 5 (Arrhenius plot) shows the activation energy (Ea) of various C_xF_y gases adsorption on the SiO_2 surface. The vertical axis shows the total number of adsorbed C_xF_y gas molecules per unit area, and horizontal axis shows reciprocal of temperature. Advanced C_5F_8 took the largest adsorption Ea value (temperature dependency is the largest), that is to say, it adsorbed easier in case of the lower temperature. In the low temperature etching process, it can be guessed that the advanced C_5F_8 gas is better than the others. Fig. 6 shows the adsorption behavior of advanced C_5F_8 gas on various surfaces at 25 degrees C. The adsorption amount on the SiO_2 surface was the largest. It was found that the adsorption amount of advanced C_5F_8 gas was greatly influenced by surfaces. The ratio of the adsorption amount on various surfaces was as follows;

photo-resist: Si: SiO_2 = 1: 5.5: 100.

Surprisingly, the adsorption amount of advanced C_5F_8 on the SiO_2 surface was 100 times larger than the photo-resist surface. Fig. 7 shows the total number of adsorbed molecules per unit area of various C_xF_y gases on various surfaces at 25 degrees C. There was no difference in the adsorption amount of C_4F_8 gas on any surface. The ratio of the adsorption amount of cyclic C_5F_8 gas on various surfaces was as follows;

photo-resist: Si: SiO_2 = 1: 1.5: 40.

It was found that advanced C_5F_8 gas had great surface selectivity between SiO_2 and photo-resist.

4. Conclusions

We clarified that the advanced C_5F_8 gas had surface selectivity between SiO_2 and photo-resist. This result shows that the advanced C_5F_8 has the best etching ability for high aspect ratio.

References

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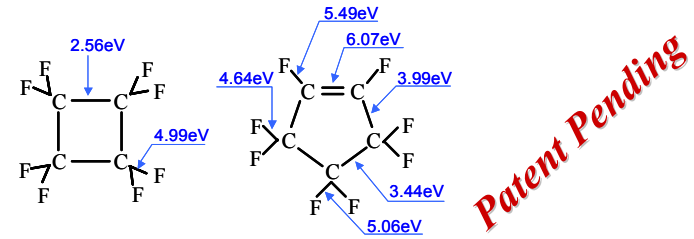

(a) C_4F_8 (b) Cyclic C_5F_8 (c) Advanced C_5F_8

Boiling point : −5.85℃
Vapor pressure
: 0.27MPa at 25℃

Boiling point : 27℃
Vapor pressure
: 0.09MPa at 25℃

Boiling point : 7℃
Vapor pressure
: 0.24MPa at 25℃

Fig. 1 Molecular structure and binding energy of various Fluorocarbon gases.

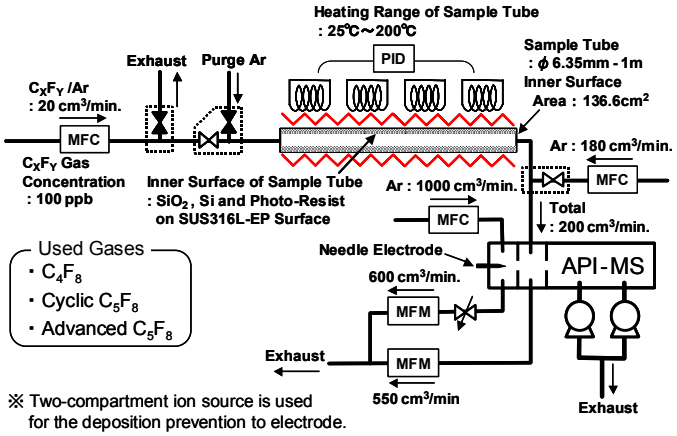

Fig. 2 Schematic diagram of the experimental setup.

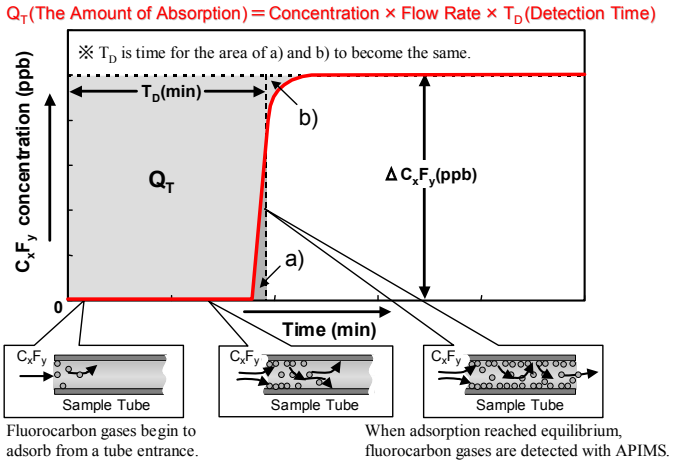

Fig. 3 Adsorption behavior model of fluorocarbon gases introduced to the various sample tubes.

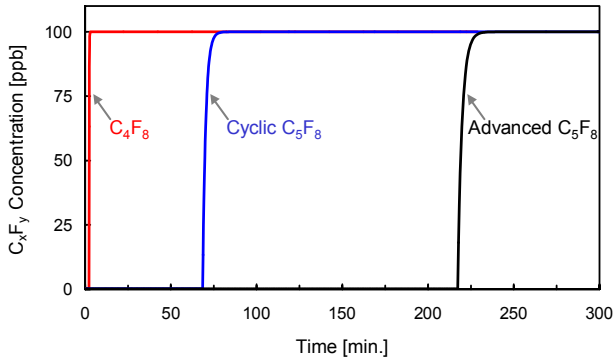

Fig. 4 Adsorption behavior of various fluorocarbon gases on the SiO_2 surface at 25 degrees C.

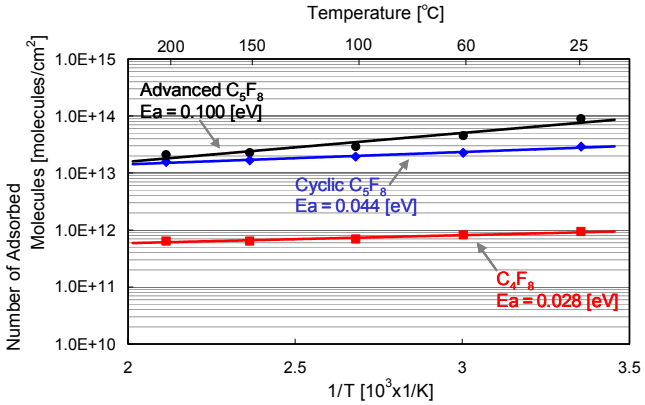

Fig. 5 Activation energy of various fluorocarbon gases adsorption on the SiO_2 surface.

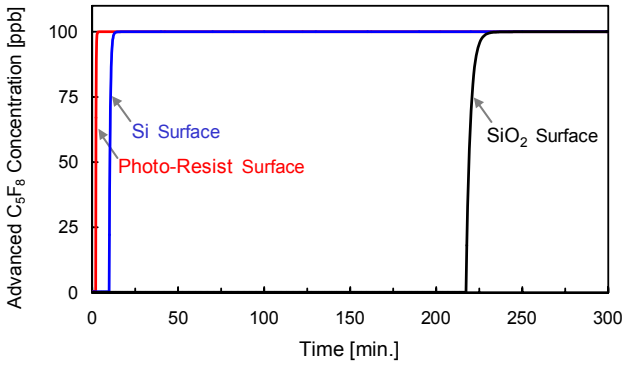

Fig. 6 Adsorption behavior of advanced C_5F_8 gas on various surfaces at 25 degrees C.

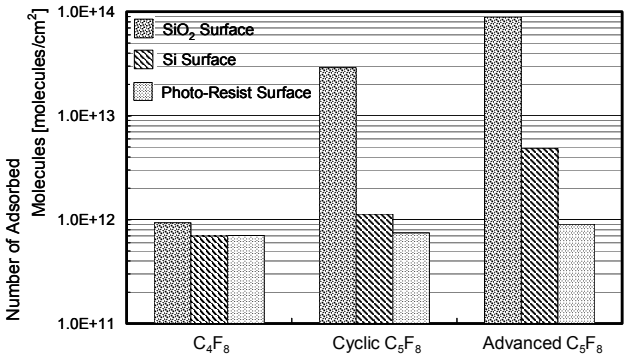

Fig. 7 The total number of adsorbed molecules of various fluorocarbon gases on various surfaces at 25 degrees C.