

# Etching Properties and Optical Emission Spectroscopy of NH<sub>3</sub> Added C<sub>5</sub>F<sub>8</sub> Pulse-Modulated ICP Plasma

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## Research Results

### 1. Introduction

Perfluorocarbons (PFCs) such as CF<sub>4</sub> and cyclic (c-) C<sub>4</sub>F<sub>8</sub>, which have been used in the dry etching of SiO<sub>2</sub>, have big global warming potentials and very long lifetimes as shown in Table 1 [1]. Recently the PFC alternative gases with small global warming potential and short lifetime are strongly required in order to protect the global environment

In this paper, excellent contact hole etching of sub-0.1 μm size in SiO<sub>2</sub> is achieved by adding NH<sub>3</sub> to c-C<sub>5</sub>F<sub>8</sub> with small greenhouse effect, and Ar mixing gas in the pulse-modulated inductively coupled plasma (ICP). The influence of the addition gas to the plasma was analyzed with the optical emission spectroscopy (OES). And correlation between flow rate of addition gas and OES is studied.

### 2. Experiments

#### 2.1 Etching system

The ICP etching system we used is schematically shown in Fig. 1. A source RF power of 13.56 MHz modulated using a function generator is introduced into the Cu ring electrode in order to control the plasma density and electron temperature independently. 400 kHz RF is used to generate substrate bias. The wafer is cooled to -11°C to suppress the etching of the resist mask. Pressure is 15 mTorr. Plasma source gas is a mixture of c-C<sub>5</sub>F<sub>8</sub> (11 sccm) and Ar (60 sccm) added with NH<sub>3</sub> (1~5 sccm). For the comparison, the effect of other adding gas such as H<sub>2</sub> or O<sub>2</sub> was investigated. The optical emission spectra from the plasma were measured to investigate the reactive species in the plasma.

#### 2.2 Sample preparation

The (100) p-Si wafers with 900 nm thick phosphosilicate-glass (PSG) layer were used for the investigation of the etching profile. The photoresist (posi-type) was patterned using electron beam lithography to investigate the several size of contact hole pattern. After etching, photoresist and deposited polymer were removed by O<sub>2</sub>-plasma and sulfuric acid/hydrogen peroxide/water mixture cleaning.

### 3. Results and Discussions

#### 3.1 Effect of addition gases

Adding oxygen to C<sub>5</sub>F<sub>8</sub>/Ar plasma greatly influences the etching profiles and selectivity (Fig. 2(a)). The oxygen addition decreases the amount of excess deposition of C<sub>x</sub>F<sub>y</sub> polymer, leading to the suppression of etch stop, but it also decreases the selectivity [4].

Adding hydrogen to C<sub>5</sub>F<sub>8</sub>/Ar plasma greatly improves the selectivity (Fig. 2(b)). The hydrogen addition decreases the amount of fluorine radicals, which induces excess etching of Si, leading to the suppression of Si etching. However, the amount of C<sub>x</sub>F<sub>y</sub> molecules is maintained, and etch stop is still caused [5].

Adding NH<sub>3</sub> to C<sub>5</sub>F<sub>8</sub>/Ar plasma can realize contact hole of sub-0.1 μm size with high aspect ratio and high selectivity (Figs. 2(c), 6). NH<sub>3</sub> in plasma generates hydrogen radicals which decrease the amount of fluorine radicals. And reaction of generated HCN and FCN may reduce the C<sub>x</sub>F<sub>y</sub> polymer [6].

#### 3.2 Optical emission spectroscopy

In order to monitor the radicals in the plasma and understand the etching mechanism, we exploited the optical emission spectroscopy (OES). Etching concerned species such as CF<sub>2</sub> (321.4nm), F (703.7nm), CN (386nm), NH (338.3nm), and H (Hα at 656nm) are monitored, and the relation between flow rate of addition gas and the intensity of luminescence was discussed.

In the case of NH<sub>3</sub> addition, the result of OES is shown in Fig. 5. The flow rate of NH<sub>3</sub> increasing, the amount of H, NH and CN (precursor of HCN, FCN) is increasing. The intensities of H, NH and CN luminescence peaks are increased but those of CF<sub>2</sub> and F luminescence peaks are slightly decreased. This result may indicate that reaction of generated HCN and FCN reduces the C<sub>x</sub>F<sub>y</sub> polymer. The C<sub>x</sub>F<sub>y</sub> polymer reduction reduces excessive protection film deposition which causes etchstop.

#### Relation to 21st COE Program

This research was performed as part of a "Fundamental Technologies for Scaled Devices".

#### Conclusions and Next Work

By addition of NH<sub>3</sub> to C<sub>5</sub>F<sub>8</sub>/Ar pulse-modulated plasma, sub-0.1 μm size and high aspect ratio (>10) contact hole etching with vertically and excellent selectivity (SiO<sub>2</sub>/Si≈80) is achieved.

This process could be used for the next generation ULSI devices (about 65 nm node MOSFET).

Furthermore, correlation between OES and etching properties is observed.

My next works are metal filling to small hole, and measuring characteristic of the device using this technique.

#### References

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[2] T. Mieno and S. Samukawa, *Jpn. J. Appl. Phys.* **34**, L1079 (1995).  
 [3] K. Takahashi *et al.*, *Appl. Phys. Lett.*, **35**, 3635 (1996).  
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 [5] L.M. Epjrath and E.J. Petrillo, *J. Electrochem. Soc.* **129**, 2282 (1982).  
 [6] T. Tokuyama, "Handoutai dry etching gijutsu", Sangyou Tosho p.73 (1992), (in Japanese).

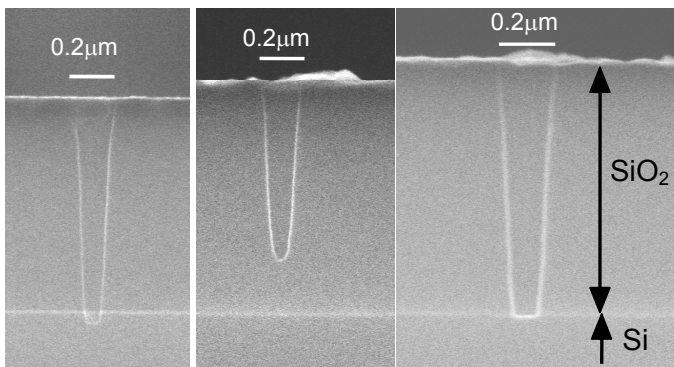
**Published Papers and Patents**

① Published Papers

M. Ooka, S. Yokoyama "SiO<sub>2</sub> Hole Etching Using

Table 1 GWP and lifetime of some etching gases.

Gas	GWP <sub>100</sub>	Lifetime (year)
CO <sub>2</sub>	1	50-1200
CF <sub>4</sub>	6500	50000
c-C <sub>4</sub> F <sub>8</sub>	8700	3200
c-C <sub>5</sub> F <sub>8</sub>	90	1



(a) O<sub>2</sub> added (b) H<sub>2</sub> added (c) NH<sub>3</sub> added  
 Fig. 2 SEM photograph of cross section of the 0.2µm contact hole etched with different addition gas.

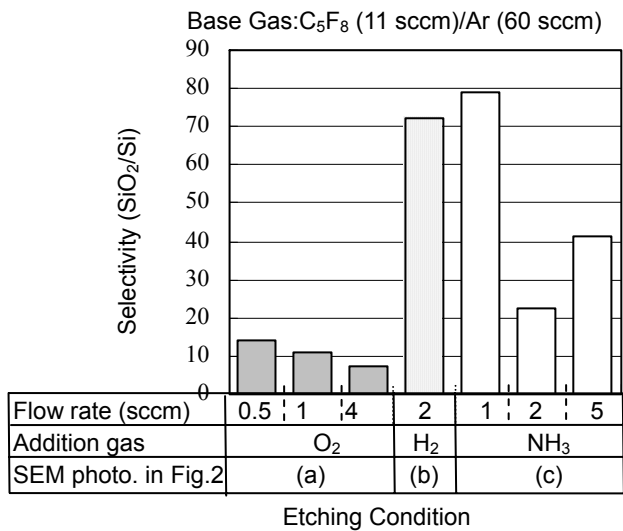


Fig. 4 SiO<sub>2</sub>/Si etching selectivity for different addition gas and flow rate.

Perfluorocarbon Alternative Gas with Small Global Greenhouse Effect": *Jpn. J. Appl. Phys.* **43** (2004) (in press).

② Proceedings

1. M. Ooka and S. Yokoyama, "Excellent Contact-Hole Etching with NH<sub>3</sub> Added C<sub>5</sub>F<sub>8</sub> Pulse-Modulated Plasma" *Extend. Abst. of the Int. Conf. on Solid State Devices and Materials (SSDM2003)* (2003) pp. 454-455.

③ Patents

Nothing.

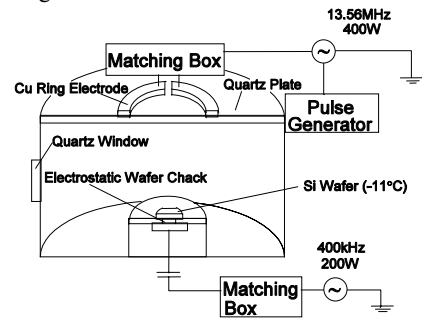


Fig. 1 Schematic diagram of ICP reactor.

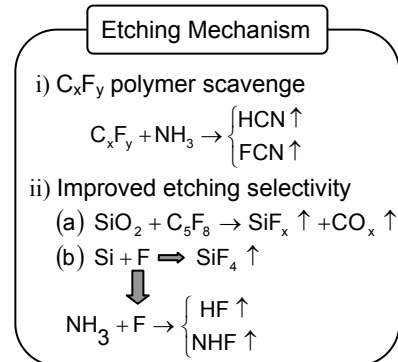


Fig. 3 Mechanism of NH<sub>3</sub> adding effect.

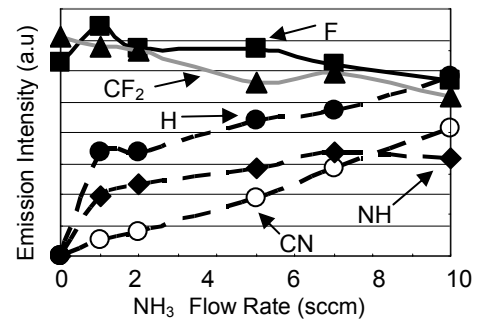


Fig. 5 OES intensity vs NH<sub>3</sub> flow rate.

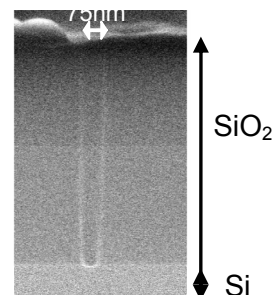


Fig. 6 SEM photograph of the cross section of the sub-0.1µm contact hole (RF ON: 50 µsec/OFF: 25 µsec, 70% over etch).