Etching Properties and Optical Emission Spectroscopy of NH₃ Added C₅F₈ Pulse-Modulated ICP Plasma

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1. Introduction

Perfluorocarbons (PFCs) such as CF_4 and cyclic (c-) C_4F_8 , which have been used in the dry etching of SiO₂, 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 μ m size in SiO₂ is achieved by adding NH₃ to c-C₅F₈ 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 late 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 $c-C_5F_8$ (11 sccm) and Ar (60 sccm) added with NH₃ (1~5 sccm). For the comparison, the effect of other adding gas such as H₂ or O₂ 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_2 -plasma and sulfuric acid/hydrogen peroxide/water mixture cleaning.

3. Results and Discussions

3.1 Effect of addition gases

Adding oxygen to C_5F_8 /Ar plasma greatly influences the etching profiles and selectivity (Fig. 2(a)). The oxygen addition decreases the amount of excess deposition of C_xF_v polymer, leading to the suppression of etch stop, but it also decreases the selectivity [4].

Adding hydrogen to C_5F_8/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_xF_y molecules is maintained, and etch stop is still caused [5].

Adding NH₃ to C_5F_8/Ar plasma can realize contact hole of sub-0.1µm size with high aspect ratio and high selectivity (Figs. 2(c), 6). NH₃ in plasma generates hydrogen radicals which decrease the amount of fluorine radicals. And reaction of generated HCN and FCN may reduce the C_xF_y 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 CF₂ (321.4nm), F (703.7nm), CN (386nm), NH (338.3nm), and H (H α at 656nm) are monitored, and the relation between flow rate of addition gas and the intensity of luminescence was discussed.

In the case of NH₃ addition, the result of OES is shown in Fig. 5. The flow rate of NH₃ 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 CF₂ and F luminescence peaks are slightly decreased. This result may indicate that reaction of generated HCN and FCN reduces the C_xF_y polymer. The C_xF_y polymer reduction reduces excessive protection film deposition which causes etchstop.

4. Conclusions

By addition of NH₃ to C_5F_8/Ar pulse-modulated plasma, sub-0.1µm size and high aspect ratio (>10) contact hole etching with vertically and excellent selectivity (SiO₂/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.

References

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Table 1 GWP and lifetime of some etching gases.

| Gas | GWP ₁₀₀ | Lifetime (year) |
|---------------------------------|--------------------|-----------------|
| $\overline{CO_2}$ | 1 | 50-1200 |
| CF_4 | 6500 | 50000 |
| c-C ₄ F ₈ | 8700 | 3200 |
| c-C ₅ F ₈ | 90 | 1 |







Fig. 4 SiO₂/Si etching selectivity for different addition gas and flow rate.



Fig. 1 Schematic diagram of ICP reactor.



Fig. 3 Mechanism of NH₃ adding effect.



Fig. 5 OES intensity vs NH₃ 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).