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Perfectly Etching Uniformity Control of Various Doped Oxide Films Using an Anhydrous HF Gas

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ABSTRACT

We have developed a perfectly etching uniformity control method of various doped oxide films using an anhydrous HF (AHF) gas. The etch uniformity and surface residues are strongly dependent on the process temperature.

With down scaling of ultra large scale integrated (ULSI) devices, the role of dry cleaning process with many benefits such as a good penetration into small size contact hole, a low cost of ownership (CoO), a drastic promotion of ESH (Environment, Safety and Health), etc., becomes even more important. It is well known that oxide film etch using AHF gas has a very high etch selectivity between soft and hard oxide in comparison with HF solution. However, two problems: a poor etch uniformity and etch residues are the dominate factor limiting all dry cleanings including AHF gas treatment. In this paper, we focus on a new method development for overcoming the issues using a AHF system in fig.1. The total gas flow rate used in this study was set to 1000 standard cubic centimeter per minute (SCCM) of a 5% diluted HF gas with ultrapure nitrogen (N_2) gas.

Figure 2 shows the dependence of BPSG film etch rate on process temperature. The etch rate of oxide film using AHF gas depends on process temperature contrary to that in HF solution. Moreover, an optimum temperature with constant etch rate of BPSG film seems to be in existence. Figure 3 shows SiF_4 peaks generated from reaction with AHF and BPSG film using a fourier transform-infrared reflectance (FT-IR) system[1]. When increasing process temperature, intensities of SiF_4 peaks are drastically decreased. This result is strongly related to the etch rate in fig.2. Figure 4 represents the etch residues after AHF treatment at high temperature. It is clear that BPSG film etch at high temperature regime has a poor uniformity and etch residues.

From these results, we suppose that BPSG film etch with process temperature can be separated by 3 kinds of regimes which are H_2O remaining regime (I), regime with a broad process window without etch residues (II), and poor etch uniformity regime with Si and P residues in fig 5. In case of regime (I), the BPSG film etch can be explained by the following reaction sequences. First, AHF gas reacts with B_2O_3 in BPSG film, resulting in making H_2O molecules. Since H_2O molecules have a high dielectric constant, it can dissolute HF gas to fluorine (F) and hydrogen (H) ions. After that, F^- ions are reacted on a successive reaction with HF molecules to generate HF_2^- ions, so that they can react with P_2O_5 and SiO_2 in BPSG film[2]. When the main ions of BPSG film etch at regime (I) are HF_2^- ions, its rate is faster than other regimes. However, H_2O generated as a by-product is difficult to exhausted to outside at low temperature regime, resulting in remaining H_2O residues on surface, so that surface rinse process is required for removing them. At the regime (III), on the other hand, H_2O molecules which were firstly formed by the reaction of AHF gas and B_2O_3 in BPSG film is easily exhausted at high temperature more than 180℃. The film etch rate is decreased because P_2O_5 and SiO_2 in BPSG film can not react with HF_2^- ions which can not be generated from the absence of H_2O and remain on film surface. Moreover, BPSG film etch by HF molecules only has a poor etch uniformity.

Figure 6 shows dependence of etch rate of various oxide films on process temperature. At optimum regime in the range of 100 to 180℃, the etch selectivity of doped and undoped oxides seem to have an unlimited value. Figure 7 shows the influence of BPSG film surface condition on etch rate. At the low temperature of regime (I), etch rate of BPSG film has a big difference with *pre-treatment*, while it is not changed irrespective of *pre-treatment* at optimum regime. We suggest that process temperature, based on the results for etch uniformity and residues of doped oxide films using AHF gas should be controlled in the range of 100 to 180℃.

A new method for perfectly etching uniformity control of various doped oxide films using an anhydrous HF gas will be presented in this article.

References

[1] N. Miki, et al., J. IEEE. ED. **37**. p107-115 (1990).
[2] T. Yabune, et al., proc. *Electrochem. Soc.* with abstract number of 1079 (1999).

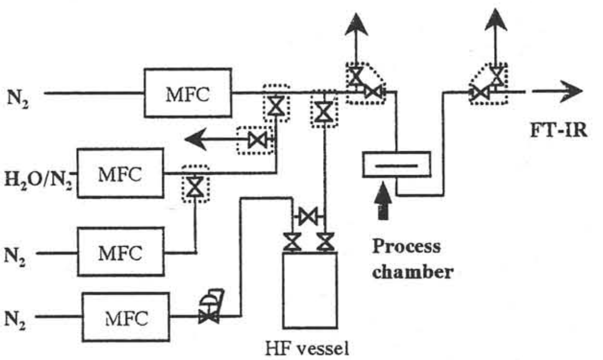


Figure 1 Schematic diagram of anhydrous HF (AHF) gas distribution system

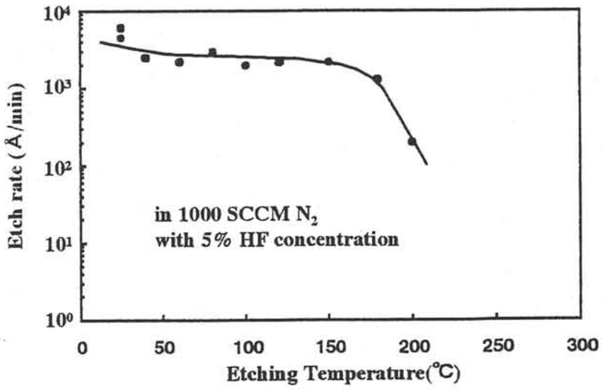


Figure 2 BPSG etch rate *vs.* temperature

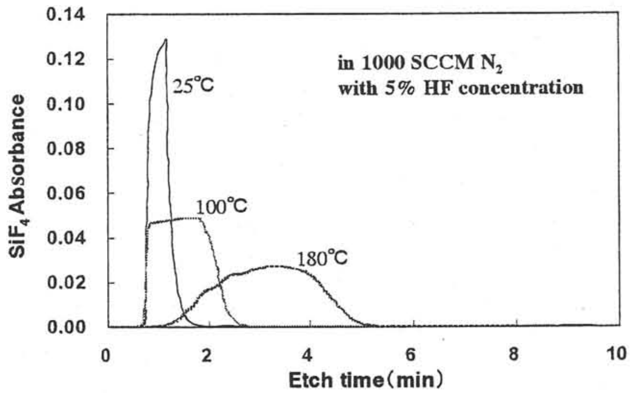


Figure 3 SiF_4 intensity in BPSG *vs.* temperature

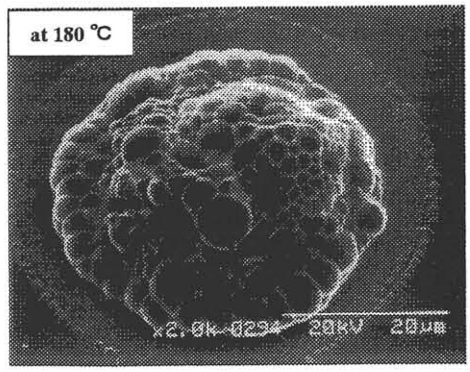
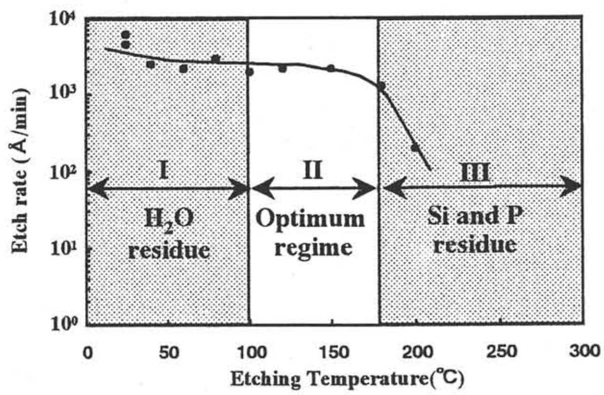


Figure 4 Etch residue after AHF treatment



I . $B_2O_3 + 6HF \rightarrow 2BF_3 + 3H_2O$

. $HF \rightarrow H^+ + F^-$ (in H_2O ambiance)

. $HF + F^- \rightarrow HF_2^-$

. P_2O_5 (in BPSG) $+ 5HF_2^- + 5H^+ \rightarrow 2PF_5 + 2H_2O$

. SiO_2 (in BPSG) $+ 2HF_2^- + 2H^+ \rightarrow SiF_4 + 2H_2O$

III . $B_2O_3 + 6HF \rightarrow 2BF_3 + 3H_2O\uparrow$ (complete)

Figure 5 Main reactions of BPSG etch using AHF gas with temperature

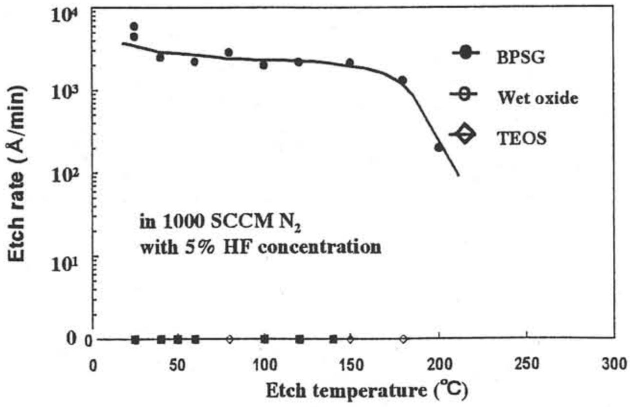


Figure 6 Etch rate *vs.* temperature

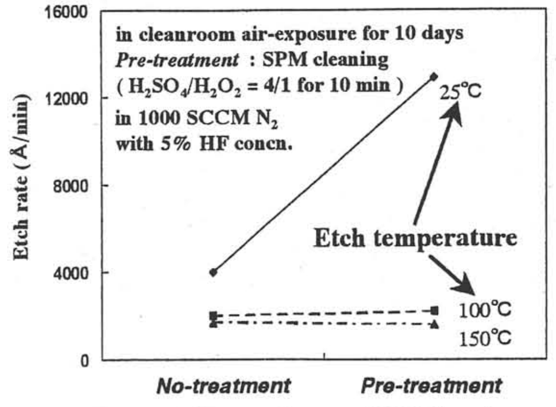


Figure 7 Dependence of BPSG etch rate on *pre-treatment*