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High Selective Etching using HF/H_2SO_4 Solution

Mami SAITO*, Hiroshi TOMITA, Kunihiro MIYAZAKI, and Soichi NADAHARA

Process & Manufacturing Engineering Center, Semiconductor Company, Toshiba Corporation
8, Shinsugita-cho, Isogo-ku, Yokohama, 235-8522 Japan.
Phone: +81-45-770-3682 Fax: +81-45-770-3577 E-mail: ma-saito@amc.toshiba.co.jp

1. Introduction

Selective etching of various SiO_2 films such as BSG and BPSG is required for many applications in ULSI manufacturing process. Practically, the etching ratio of those films to thermal SiO_2 film is required at the range of 50 to 200. For achieving high selectivity, single wafer etching system using anhydrous HF vapor is well known in this field[1,2]. The etching rate of oxides is controlled by HF constituents, which are dissociated in H_2O vapor at optimum temperature. However, it takes longer time as doped oxide films become thicker.

It is also necessary to minimize HF_2^- formation, on which thermal SiO_2 etching strongly depends, in order to realize high selectivity in batch system. Recently, new etching solution with low dielectric constant is commercially available to suppress HF dissociation. However, these kinds of etching solution must be handled carefully, because they are consisted of organic solvent.

In this study, we applied H_2SO_4 as a solvent, and anhydrous HF or $NH_4F\cdot HF$ was added as an etchant. The mechanism of high selective etching by using those etching solutions is described in following sections. Finally, this high selective etching is realized in batch system and is demonstrated for a hard mask removal in deep trench process.

2. Experimental

H_2SO_4 was used as a solvent because water content in H_2SO_4 is only 2-4wt%. Also, anhydrous HF or $NH_4F\cdot HF$ crystal was selected as an etchant, which was added in H_2SO_4 without increase of water content.

Thermal SiO_2 and BSG films were etched in a wet batch system using 94-98wt% H_2SO_4 with 0.5-2wt% of anhydrous HF or $NH_4F\cdot HF$ crystal at 30-90℃. Film thickness before and after etching was measured by ellipsometry. Etching rates and selectivity (BSG/SiO_2) were obtained under the various etching conditions.

3. Results and Discussion

3-1. Selective Etching using H_2SO_4 as a Solvent

First of all, the etching rate and the selectivity of oxides were investigated under the several conditions in the mixture of H_2SO_4 and anhydrous HF. Figure 1 shows the H_2O concentration dependence of etching rates of both films and selectivity when the HF concentration was 2wt% and the temperature wais 90℃. The result shows that the etching rate of both films increased with the increase of the H_2O content. On the contrary, the selectivity decreased as the increase of the H_2O content. Therefore, the H_2O concentration needs to be controlled less than 4wt% to keep high selectivity over 100.

Next, the HF concentration dependence of both etching rates and selectivity, when the H_2O content was 2wt%, was investigated at 90℃ as shown in Fig. 2. Although the etching rate of both films increased with the HF concentration, the etching rate of the BSG film depended on the HF concentration than that of the thermal SiO_2 film. The reason is that the HF dissociation hardly proceeds when H_2O concentration is very low. Thus, the selectivity increased with the HF concentration and it achieved over 200 when the HF concentration was more than 1wt%.

Figure 3 shows the temperature dependence. It is found that the selectivity becomes the maximum at 60℃. Although the etching rates increased with process temperature, the selectivity keeps over 100.

3-2. Comparison of Anhydrous HF and $NH_4F\cdot HF$

As described before, in order to realize high selective etching, the etching must be carried out under the condition of low water concentration as much as possible. Then anhydrous HF and $NH_4F\cdot HF$ were applied as an etchant and both effects to selective etching were discussed. Figure 4 shows the difference of the selectivity between HF and $NH_4F\cdot HF$, which were added in 98wt% H_2SO_4. At 90℃, the selectivity in the HF/H_2SO_4 solution is about 1.5 times higher than that in the $NH_4F\cdot HF/H_2SO_4$ solution. This result means that the ratio of HF to HF_2^- in the HF/H_2SO_4 solution is 1.5 times higher than that in the $NH_4F\cdot HF/H_2SO_4$ solution under the same etching rates of BSG films.

In compliance with equations (1) and (2), HF dissociation in H_2SO_4 strongly depends on H_2O concentration. On the other hand, $NH_4F\cdot HF$ is easily dissociated to HF_2^- (Eq.(3)).

$$HF + H_2O \Leftrightarrow H_3O^+ + F^- \quad (1)$$

$$HF + F^- \Leftrightarrow HF_2^- \quad (2)$$

$$NH_4F\cdot HF \Leftrightarrow NH_4^+ + HF_2^- \quad (3)$$

Photos. 1 (a) and (b) show the SEM images before and after selective etching using HF/H_2SO_4 in a hard mask (BSG) removal of deep trench process. It is clearly shown that the BSG film can be etched in high selectivity without etching pad-SiO_2 films.

4. Conclusions

The key point for realizing a high selective etching is a control of water concentration in etching solution. When water content in H_2SO_4 solution is low, less than 4wt%, high selective etching is realized. Although both HF and $NH_4F \cdot HF$ are effective as an etchant, HF is more effective and it shows high selectivity with keeping high etching rate. This technique using H_2SO_4 does not need special wet batch system; it is possible to use traditional wet system.

Acknowledgments

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References

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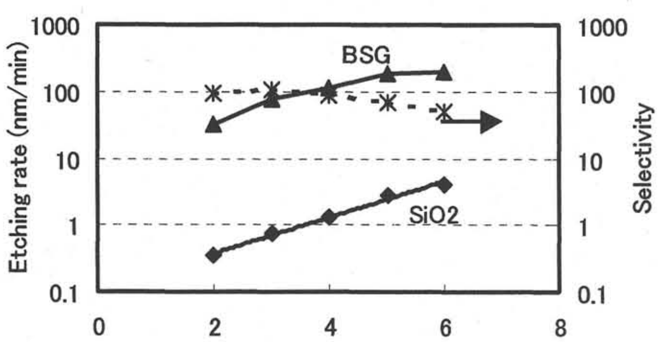


Fig. 1 H_2O concentration dependence of etching rate and selectivity (BSG/SiO_2)

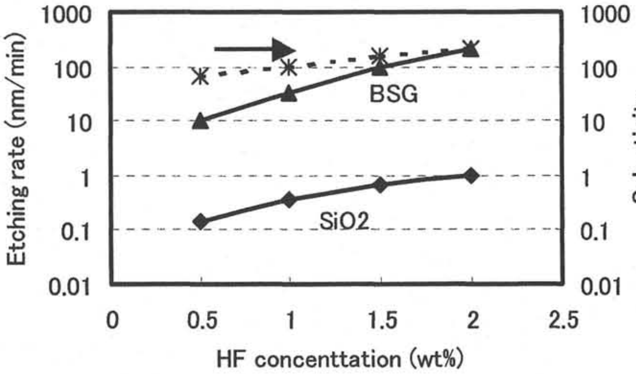


Fig. 2 HF concentration dependence of etching rate and selectivity (BSG/SiO_2)

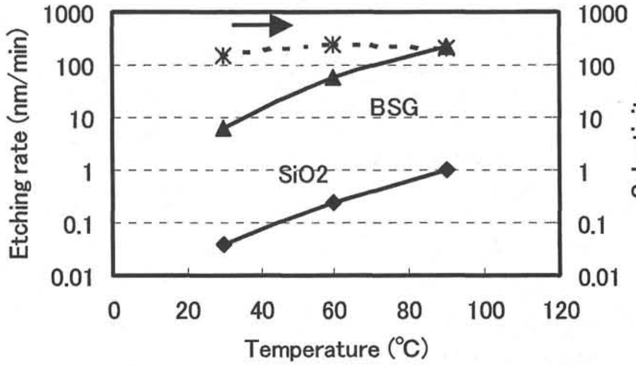


Fig. 3 Temperature dependence of etching rate and selectivity (BSG/SiO_2)

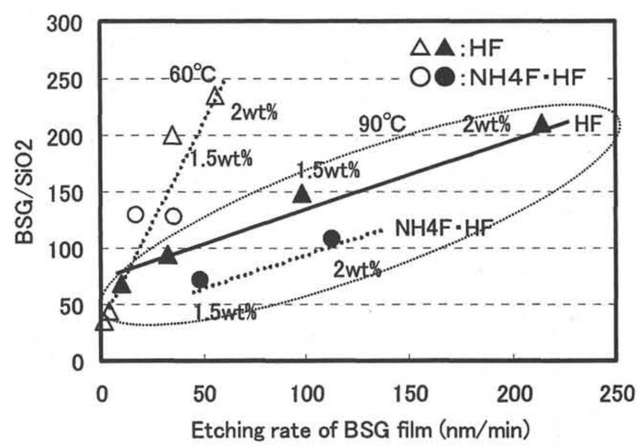
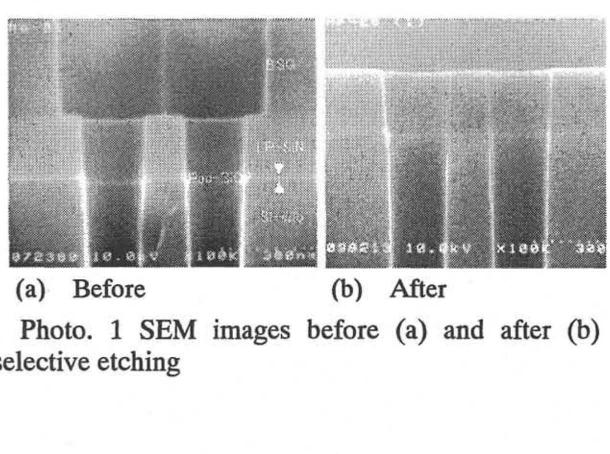


Fig. 4 Comparison of anhydrous HF and $NH_4F \cdot HF$



(a) Before (b) After

Photo. 1 SEM images before (a) and after (b) selective etching