# A New Cleaning Method by Using Anhydrous HF/CH<sub>3</sub>OH Vapor System

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For wafer surface cleaning technology, a new etching process of  $SiO_2$  film by anhydrous HF/CH<sub>3</sub>OH vapor system was investigated intensively. Especially CH<sub>3</sub>OH was used as a solvent for HF instead of conventional H<sub>2</sub>O. And we could attain to improve the selectivity ratio of oxide etching (native oxide/BPSG), and to suppress the native oxide growth and particle generation after etching. This HF/CH<sub>3</sub>OH vapor etching system is hopeful as a pre-cleaning method of gate oxidation, CVD and epitaxial growth.

### 1.INTRODUCTION

For wafer surface cleaning technology, the vapor phase etching system has been developed by many researchers. $^{1/2}$  This vapor phase system is suitable for the fine trench and contact holes with high aspect ratio. In order to clean the wafer surface effectively, it is necessary to etch oxide film selectively and to suppress the native oxide growth and particle generation. But this goal can not be realized by the conventional HF/H20 vapor etching method. On the other hand. F.J.Grunthaner and P.J.Grunthaner also investigated to etch silicon oxide film by using the liquid mixture of anhydrous HF and alcohol (  $C_2H_5OH$  ). From the point of their method and etching reaction mechanism, however, no detectable differences could be found compared with the etching method using  ${\rm HF}$  aqueous solution.  $^{(3)}$ 

In this work we investigated a new etching process for oxide film by anhydrous  $HF/CH_3OH$  vapor system. Especially  $CH_3OH$  in vapor phase was used as a solvent for HF replacing conventioal  $H_2O$ . And we intended to improve the selectivity ratio of oxide etching, and to suppress the native oxide regrowth and particle generation after etching.

#### 2. EXPERIMENTAL

The single wafer vapor etching chamber for  $HF/CH_3OH$  vapor system is equipped with the supply of N<sub>2</sub> gas as carrrier, the mixture of HF and CH<sub>3</sub>OH vapor as etching species, and CH<sub>3</sub>OH vapor for controlling the concentration of vapor mixture as shown by Fig.1. The source liquid are the mixture of HF and CH<sub>3</sub>OH, and CH<sub>3</sub>OH respectively. Each source liquid is bubbled with N<sub>2</sub> gas and the vapor is introduced into the etching chamber. The mixture of HF and  $CH_3OH$  used in this experiment is azeotropic state, in which the concentration ratio of vapor phase is equal to the one of liquid phase, and the concentration of HF and  $CH_3OH$  is 38.5 wt% and 61.5 wt% respectively. By using the mixture of HF and  $CH_3OH$  in azeotropic state, we can control the supply of vapor steadily. This system which are pipe, chemical tanks, etching chamber and so on consists of fluoric resin.

The sample wafers are 10-15 ohm-cm ntype (100) oriented single crystal silicon, 5 inches in diameter. The oxide film about 140 A in thickness was formed on silicon wafers by the ordinary dry O<sub>2</sub> oxidation at 950 °C. BPSG film was deposited on wafers by ordinary low pressure CVD about 2000 Å in thickness. In order to remove organic contamination and  $H_2O$  adsorbed on wafer surface, all sample wafers were irradiated UV-ray in air for 3 minutes before etching reaction by using low pressure mercury-lamp, and native oxide was also grown on bare wafer surface about 10 Ă thickness. The etching rate of native Si02



Fig.1 Schematic diagram of HF-CH<sub>3</sub>OH vapor cleaning apparatus





Fig.2 Native SiO<sub>2</sub> etching rate by HF and  $CH_3^2OH$  vapor



Fig.3 BPSG film etching rate by HF and  $\rm CH_3OH$  vapor

film and BPSG film was evaluated by changing HF and  $CH_3OH$  concentration. When thermal  $SiO_2$  film was etched, the number of particles was counted. Surface condition was analyzed by ESCA. The etching condition is at 22°C and under the atmospheric pressure.

## 3.RESULTS AND DISCUSSION

The etching rate of native oxide and BPSG film were examined by  $\rm HF-CH_3OH$  vapor system. Total N<sub>2</sub> carrier gas flow rate is 10 SLM, which is the amount of (a) and (b) SLM.

The symbol (a) represents the  $N_2$  gas flow rate through the upper route in Fig.1, and (b) represents the  $N_2$  gas flow for bubbling HF and CH<sub>3</sub>OH mixture. The results, shown in Figs. 2 and 3, show a marked increase in the etching rate as the  $N_2$  gas flow rate for bubbling HF and  $CH_3OH$  mixture, in other words, the concentration of HF is incrased. And then, the etching rate was controlled by CH<sub>3</sub>OH concentration. In the case of high CH<sub>3</sub>OH concentration, in which N<sub>2</sub> carrier gas is enriched with CH<sub>3</sub>OH by bubbling, the etching rate of BPSG film decreased to under 200 A/min., and the etching rate of native oxide increased to over 10 A/min. The etching selectivity ratio ( native oxide/BPSG ) is over 1/20 in the process of HF/CH<sub>3</sub>OH vapor system. This selectivity ratio is better than the case of  $\rm HF/H_2O$  vapor 1/100-1/200. And the HF/CH3OH vapor system is hopeful for contact hole cleaning.

The native oxide growth after etching process was suppressed effectively by the HF/CH<sub>3</sub>OH vapor etching method. From ESCA measurement, peak around 104 eV of Si<sub>2p</sub> spectra coresponding with native oxide disappeared after HF/CH3OH vapor cleaning. Fig.4 shows this result compared with the case of wet etching by HF aqueous solution. In order to evaluate the thin oxide film on wafer surface, the condition of take-off angle was 20°. After rinsing the wafer with D.I. water following etching, Si<sub>2p</sub> peak about 104 eV appeared. This can be attributed to the regrowth of native oxide film on silicon wafer owing to H<sub>2</sub>O. Carbon contamination after HF/CH<sub>3</sub>OH vapor cleaning was not more than after wet etching by using HF aqueous solution from measurement of ESCA C<sub>1s</sub> spectra.

Fig.5 shows the particle counts over



Fig.4 Si<sub>2p</sub> ESCA spectra after etching native oxide.

0.28µm size after etching thermal oxide film (140Å) by changing  $N_2$  gas flow rate (a) through the upper route in Fig.1 at 22°C.  $N_2$  gas for bubbling (HF/CH<sub>3</sub>OH) mixture or (HF/H<sub>2</sub>O) mixture is 1 SLM. Total  $N_2$  gas flow is (1+a) SLM. The number of particle generation in the case of HF/CH<sub>3</sub>OH vapor system was remarkably decreased than the case of HF/H<sub>2</sub>O vapor system. And particle counts decreased with the increasing of the  $N_2$  gas flow rate for dilution of HF containing vapor.

Etching species of  $HF/CH_3OH$  vapor system should be produced as follows.<sup>4</sup>

 $2HF + CH_3OH \longrightarrow HF_2^- + (CH_3OH)H^+$ 

This dissociation reaction is analogous to  $\rm HF/H_{2}O$  system.

 $2HF + n(H_2O) \longrightarrow (H_2O)_nH^+ + HF_2^-$ 

Silicon oxide film is etched by HF2 species as the case of HF/H<sub>2</sub>O system. In the case of high CH3OH concentration, the etching rate of BPSG film decreased and the etching rate of native oxide increased compared with the case of low CH<sub>3</sub>OH concentration. This etching characteristic may be depending on the using of CH<sub>3</sub>OH vapor. In the case of high CH<sub>3</sub>OH concentration, ionization of HF will be promoted and the concentration of  $\mathrm{HF}_2$  species will be large, 4) so the etching rate of native oxide increased. On the other hand BPSG film is liable to absorb H20. And H20 produced by the etching reaction is exhausted accompanying with CH<sub>3</sub>OH vapor which have affinity with  $H_20$ . So the etching rate of BPSG film decreased in the case of high CH<sub>3</sub>OH concentration. These etching results should





be appeared because  $\mathrm{H}_2\mathrm{O}$  in the etching process is reduced.

 $\rm H_20$  and  $\rm O_2$  in the etching reaction cause the growth of native oxide on wafer surface.<sup>5)</sup>  $\rm H_20$  promote the oxidation of silicon surface. Because the concentration of  $\rm H_20$  and  $\rm O_2$  during etching reaction is reduced in the HF/CH<sub>3</sub>OH system, the re-oxidation of bare silicon surface after HF-CH<sub>3</sub>OH vapor etching is suppressed.

SiF<sub>4</sub>, which is the product of SiO<sub>2</sub> etching reaction, will react with  $H_2O$  and change into SiO<sub>2</sub> and  $H_2SiO_3$ . This product is considered to be a cause of particle. Reducing  $H_2O$  in reaction system by using CH<sub>3</sub>OH vapor, the generation of these non-volatile products can be suppressed.

In the silicon oxide etching process, it should be noted as follows.

\*  $H_2O$  content in the reactive agent vapor is reduced by using  $CH_3OH$  instead of  $H_2O$ .

\*  $H_20$  produced by the etching reaction is exhausted accompanying with  $CH_3OH$  vapor which have affinity with  $H_20$ . And it is necessary to avoid forming the condensed layer of etching chemicals on the wafer surface which absorb  $H_20$  produced by the etching reaction.

\* Before etching reaction H<sub>2</sub>O adsorbed on wafer surface should be removed by drying.

By removing the influence of  $H_2O$  as mentioned above, the effective results which are the good selectivity ratio of etching and the suppression of particle could be obtained in the HF/CH<sub>3</sub>OH vapor system.

This HF/CH<sub>3</sub>OH vapor etching system is promising as a pre-treatment of gate oxidation, CVD and epitaxial growth.

### 4.CONCLUSION

By using HF/CH<sub>3</sub>OH vapor system, we could achieve to improve the selectivity ratio of oxide etching ( native oxide/BPSG ), and to suppress the native oxide growth and particle generation after etching. By removing the influence of  $H_2O$ , these effective results were obtained.

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