Extended Abstracts of the 1993 International Conference on Solid State Devices and Materials, Makuhari, 1993, pp. 627-629 **PC-2-12**

Multipurpose Cleaning by $H_2SO_4/H_2O_2/HF$ Solution

T. OHNISHI, M. ENDO, K. YANO and N. NOMURA

Semiconductor Research Center
Matsushita Electric Industrial Co., Ltd.
Moriguchi, Osaka 570, Japan

We propose a new H_2SO_4 / H_2O_2 / HF solution for removing both particles and contaminants. The incorporation of HF in H_2SO_4 / H_2O_2 solutions is very effective in removing particles as well as organic contaminants. From the oxide breakdown field measurements, the H_2SO_4 / H_2O_2 / HF solution demonstrates excellent particle removal characteristics comparable to that of NH_4OH / H_2O_2/ H_2O solutions and shows improved residue removal ability compared to the conventional H_2SO_4 / H_2O_2 solutions.

1. Introduction

In today's VLSI fabrication, clean surface technology is a key for improving device performance and production yield. To obtain contamination-free surfaces, it is common to use specific cleaning solutions for specific purposes. For example, H_2SO_4 / H_2O_2 (Sulfuric acid, hydrogen Peroxide Mix; SPM) solutions are used for removing organic and metal contaminants and NH_4OH / H_2O_2 / H_2O (Ammonium hydroxide, hydrogen Peroxide Mix; APM) solutions are used for particle removal [1]. As it is difficult to take away particles by the SPM solution as shown in Fig. 1, there is no solution for removing contaminants and particles at the same time. From manufacturing stand point of view, however, it is highly desired to provide contamination-free surfaces with lesser cleaning process steps.

In this paper, we introduce a new H_2SO_4 / H_2O_2/ HF solution for multipurpose cleaning and discuss the results of its cleaning characteristics.

2. H_2SO_4 / H_2O_2 / HF (SPFM) solution

For removing organic contaminants, SPM solutions are used at high temperature. The erosion of the substrate is very effective in removing particles. For removing particles as well as organic and metal contaminants by a single dip, however, the erosion of SiO_2 films by the cleaning solution must be controlled within several nanometer at high temperatures. Table I shows the reaction in SPFM solutions[2]. In general, SiO_2 dissolves into SiF_6^{2-} under 60℃ and is dissociated to SiF_4 gas over 60℃ in a HF solution. Therefore, SPFM solution is likely to have a cleaning condition with a suitable SiO_2 etching rate at high temperature.

3. Experimental

In order to identify appropriate etching conditions, etch rates for thermal SiO_2 were characterized at various temperatures and HF concentrations in a SPM solution by an ellipsometric method. The efficiency of particle removal was characterized by the standard oxide breakdown field measurements on MOS capacitors, where the SPFM solution was used before growing a 11nm-thick thermal SiO_2. The MOS capacitors had n+ polysilicon gates with an area of $30mm^2$. In addition, the residue removal ability of the SPFM solution was observed on polysilicon structures immediately after reactive ion etching (RIE) using an SEM.

4. Results and Discussions

Figure 2 shows the oxide etch rates for 0.01%HF and 1% HF as a function of temperature. The etch-rate curves are divided into three temperature regions, (I) 20-60℃, (II) 60-130℃ and (III) >130℃. These regions are explained by individual reactions as listed in Table I [2]. From the above results, desired etching conditions having the etching rates of 0.1-1nm / min can be obtained in the temperature region II in Fig. 2 by adjusting the HF concentration.

SiO_2 films are not etched over 130℃ as shown in Fig. 2. In order to verify the existence of the reaction (3) in Table I, we etched SiO_2 films with SPFM solution at room temperature, with progressive addition of H_2O. The equilibrium reaction (3) shows that HF is consumed to form HSO_3F. HSO_3F is inert against etching SiO_2. As shown in Fig 3, the etch rate is increased in proportion to the amount of additional H_2O. SiO_2 films are etched by HF produced from hydrolysis of

HSO_3F. As a result, the equilibrium reaction (3) is verified by addition of H_2O.

In Figure 4, distribution of breakdown events in the MOS capacitors cleaned by the SPFM solution is compared with those cleaned by the SPM or the APM solution. The breakdown voltage is defined as a voltage when the current intensity through the SiO_2 films reached a value of 1.0×10^{-4} A/cm^2. In terms of yield of the MOS capacitors, the result of the SPFM solution is comparable to that of the APM solution. The new solution removes particles as efficiently as the APM solution.

Figure 5 shows the SEM photographs of RIE-etched patterns of a 800nm thick polysilicon on SiO_2 after the cleaning by (a) conventional SPM solution and (b) the SPFM solution. The SPFM solution removes the residue films which would persistently remain after conventional SPM cleaning. This effect is attributed to the optimized SiO_2 etching rate of the SPFM solution.

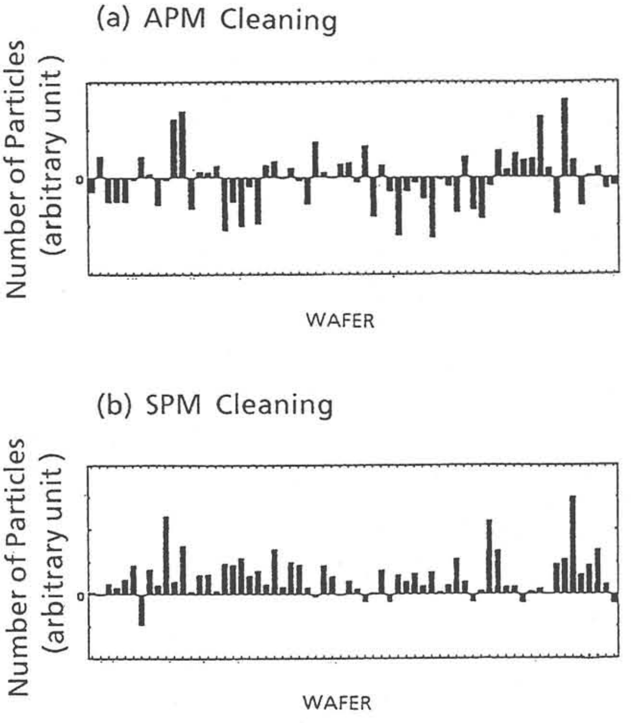

Fig. 1 Trend of the number of particles on silicon wafer surface in (a) APM cleaning and (b) SPM cleaning. These figures show the number subtracted the value of particles before cleaning from that after cleaning.

5. Conclusions

A multipurpose H_2SO_4 / H_2O_2 / HF solution has been developed. The H_2SO_4 / H_2O_2 / HF solution demonstrated excellent particle removal characteristics comparable to that of NH_4OH / H_2O_2 / H_2O. Moreover, this solution improved residue removal ability compared to conventional H_2SO_4 / H_2O_2 solution. This new cleaning solution is likely to improve yield and reduce cleaning process steps in VLSI fabrication.

6. References

1) W. Kern, J. Electrochem. Soc., 137 (1990), 1887
2) Y. Shibata et al., in "Inorganic Chemistry Works III (Mukikagakuzensyu III in Japanese), Maruzen, Tokyo (1958).

Table I Important reaction equations in SPFM solutions[2].

No.	Temperature region	Reaction equation
(I)	Below 60°C	$SiO_2 + 6HF \rightleftharpoons H_2SiF_6 + 2H_2O$
(II)	60~100°C	$SiO_2 + 4HF \rightarrow SiF_4 \uparrow + 2H_2O$
(III)	Above 130°C	$H_2SO_4 + HF \rightleftharpoons HSO_3F + H_2O$

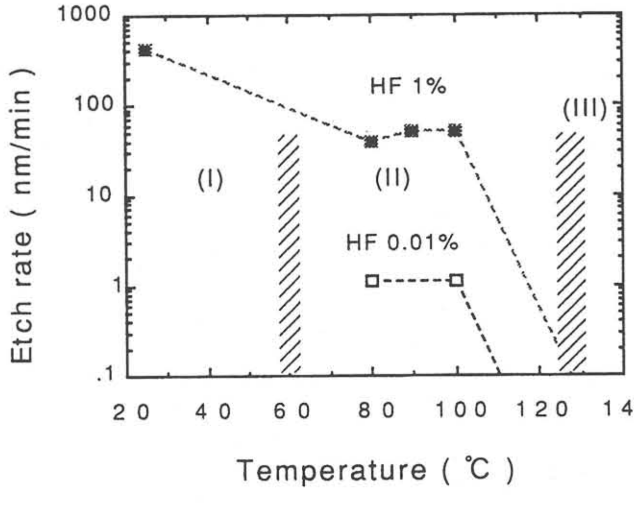

Fig. 2 Etch rates for 0.01%HF and 1%HF as a function of the temperature.

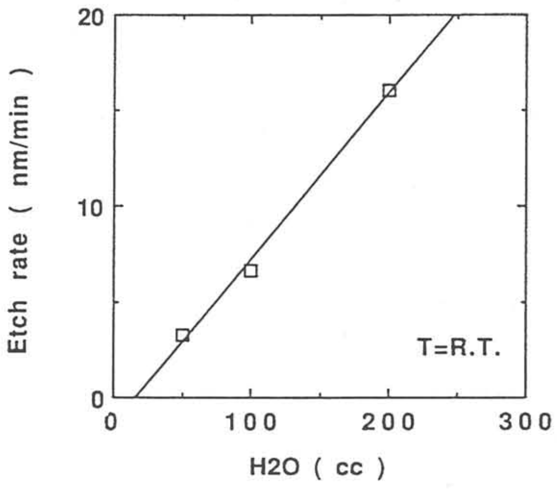

Fig. 3 Etch rates for H_2SO_4 / H_2O_2 / HF as a function of the amount of additional H_2O.

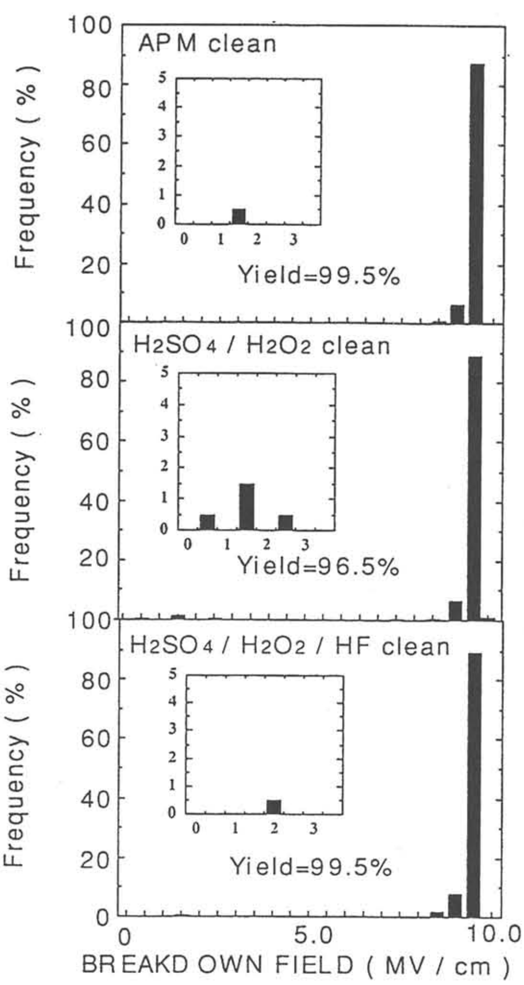

Fig. 4 Distribution of oxide breakdown events in MOS capacitors fabricated using three different cleanings.

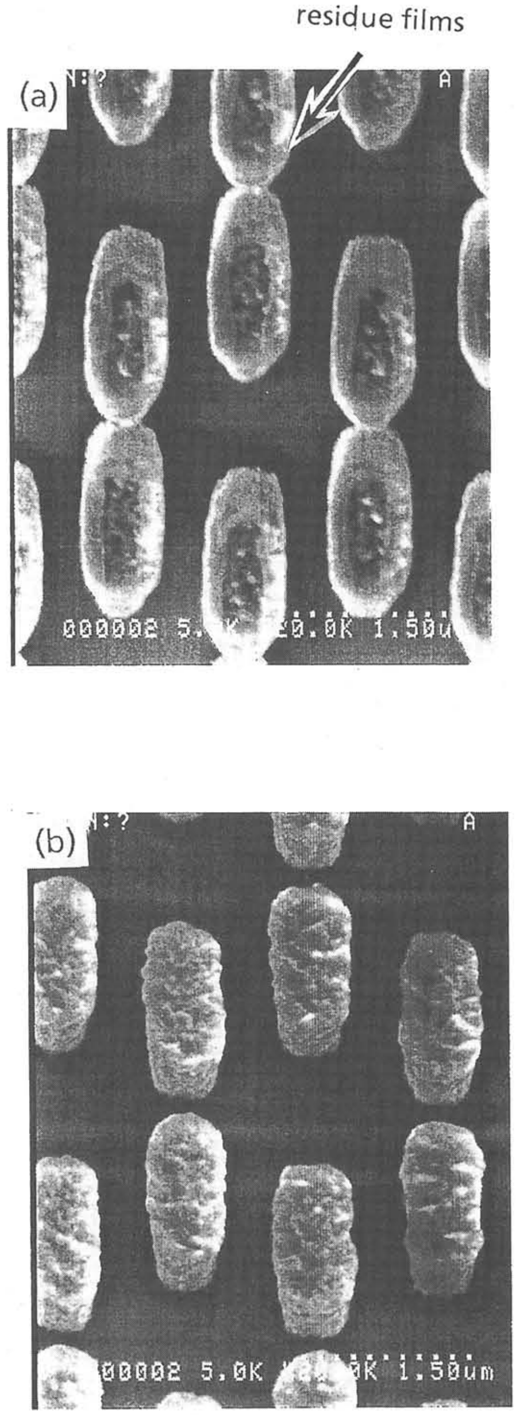

Fig. 5 SEM photograph of etched patterns in (a) SPM cleaning and (b) SPFM cleaning.