Extended Abstracts of the 2000 International Conference on Solid State Devices and Materials, Sendai, 2000, pp. 174-175

A-4-5

Strategy in Cleaning Processes for Future Materials

Geun-Min Choi, Francesco Pipia, and Tadahiro Ohmi

Department of Electronic Engineering, Graduate School of Engineering,
Tohoku University, Sendai, Japan
Fax: +81-022-263-9395, Phone: +81-022-217-7124, E-mail: choi@sse.ecei.tohoku.ac.jp

ABSTRACT

This study was carried on to understand future cleaning issues and suggest strategy in cleaning processes for future materials. It shows that conventional cleaning solutions such as SPM, SC-1, SC-2, etc, that are widely used in manufacturing device [1], have a high etch rate on new materials, so that they cannot be applied to surface cleaning of new materials irrespective of contaminants removal efficiency such as particles, organics, metallic impurities, etc. Additionally, new materials in table 1 also show a strong dependence of etch rate on pH and oxidation-reduction potential (ORP) values in solution, so that it is practically required to pay much attention when selecting the chemical solution.

Figure 1 represents the dependence of the etch rate of various metal films on cleaning solutions. The etch rates on metals such as copper (Cu) , aluminum (Al), and tungsten (W) are very fast and strongly depend on chemical solution, while platinum (Pt) film with a high electronegativity is not etched in all three solutions. Figure 2 illustrates the dependence of various film etch rates on pH and ORP values in UPW. Those values were controlled by adding HCl or NH_4OH to UPW. Cobalt (Co) film has a high etch rate in acidic solution, while Al etch rate is drastically increasing in alkali solution. Therefore, solutions should be diluted to reduce etch rate during cleaning. Table 2 shows the chemical strategies and goals for new material cleaning, according to our results. In order to apply new chemicals to future materials surface cleaning, low etch rate and no surface damage is firstly requested in comparison with the conventional cleanings that were just focused on a contamination-free surface, an impressive cost reduction for cleaning, and promotion of ESH (Environment, Safety and Health). Even though chemical has an excellent cleaning efficiency as well as a low cost of ownership (CoO), chemicals with high etch rate cannot be introduced to new material cleaning. Therefore, the etch rate of film should be added to the chemical requirements for substrate cleaning. In order to meet these requirements, the authors suggest two solutions: acid or alkali solution added to O_3-UPW (in fig.3) and surfactant added to HF solution (in fig4).

Figure 3 shows the dependence of etch rate of various films on pH and ORP values in an ozonated ultrapure water (O_3-UPW) which is well known to achieve excellent results in removing particles and organic contaminants [2]. According to our analysis on etch rate values, though, the pH value needs a tight and precise control to satisfy the requirement introduced above, and hence to keep the etched thickness into reasonable intervals. Figure 4 shows the influence of surfactant in *HF-based* solutions on the etch rate of various films. Two solutions, namely FPM (a hydrofluoric acid-hydrogen peroxide mixture) and FPMS (a hydrofluoric acid-hydrogen peroxide mixture with non-ionic surfactant) were used to study the etch rate of films. It has been clearly found that the etch rates of various metals as well as oxide films do not strongly depend on adding surfactant to solution which a meaningful influence is obtained on silicon surfaces such as crystalline-, poly-, and a-Si films. FPMS only without megasonic irradiation does not have particle removal efficiency on silicon surface, since silicon etch rate by adding surfactant is drastically decreased In contrast, in the situation in which both oxide and metal layers have to be cleaned in the same time, FPMS is a good candidate. In fact, as shown in fig. 4, both oxides and metals have nearly same etch rate irrespective of surfactant addition into *HF-based* solution, while surfactant presence can establish the same polarity of zeta potential between particles and substrate. Therefore, the *HF-based* solutions with etch capability of substrate and same zata potential polarity between particles and substrate by surfactant can have excellent particle removal efficiency on metals and/or oxide exposed surface.

we will suggest new chemicals that can applied to oxides, metal films, and new materials in this article.

References

[1] W. Kern and D. A. Puotien, RCA Rev., **31**, (1970) 187.
[2] T. Ohmi et al., J. Electrochem. Soc. **140**. (1993) 804.
[3] T. Ohmi et al., Proc. SWPCC. (2000) 1

Module		Current	Candidate
Word line (W/L)		* P-doped Si + WSi_2 (* P : Phosphrous)	.W/WN/WSi_2 . Ti/TiN/$TiSi_2$. Co/$CoSi_2$
Bit line (B/L)		P-doped Si	. W/WN/WSi_2
Capacitor	Electrode	P-doped Si	. Ti/TiN,Ru,Pt,Ir . TiAlN, TaAlN, W/WN
	Dielectrics	Nitrde/oxide	. Ta_2O_5, STO, BST, SBT, PZT
Metal line		Al, W	. Cu, W, Al

Table 1 New materials for future device fabrication

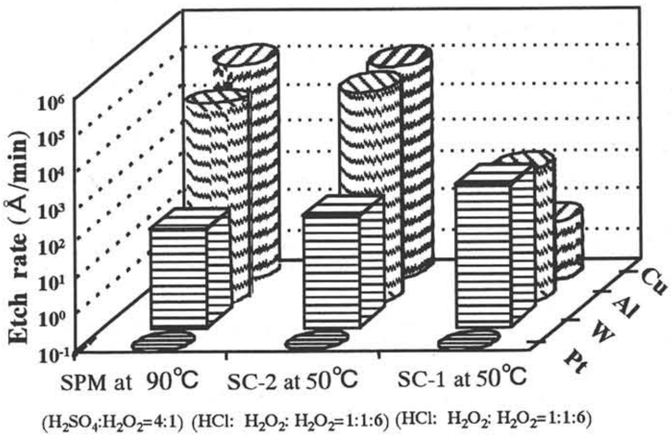

Fig. 1 Etch rate *vs.* conventional cleaning

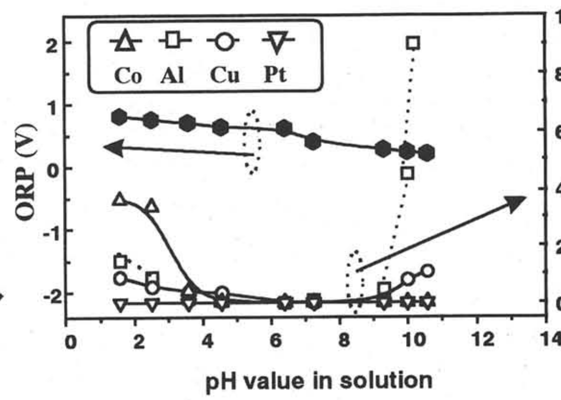

Fig.2 Etch rate *vs.* pH & ORP value in UPW

1. **Low etch rate and no surface damage**
2. **Particles & organic impurities removal efficiency**
3. **Cleaning without using megasonic irradiation**
4. **Universal chemical: the same for ALL materials**

Table 2 Strategies and goals for new material cleaning

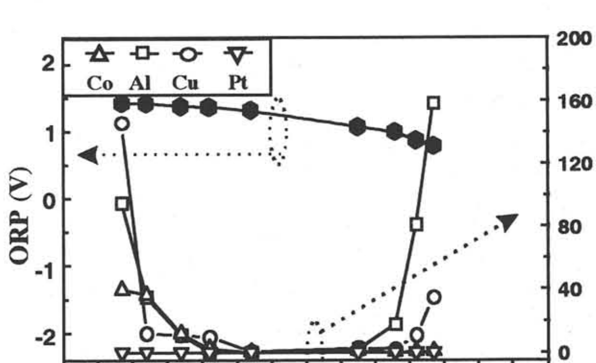

Fig.3 Etch rate *vs.* pH & ORP values in O_3-UPW

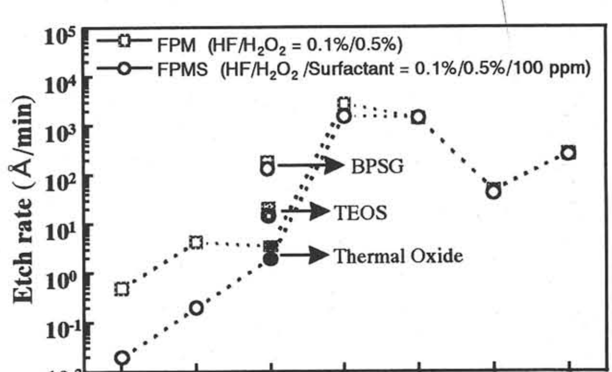

Fig.4 Etch rate *vs.* surfactant effect in FPM solution