

A modified multi-chemicals spray cleaning process for post-CMP cleaning application

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Abstract

Chemical mechanical planarization (CMP) has become widely accepted for the planarization of device interconnect structures in deep sub-micron semiconductor manufacturing. Attractive features of CMP include (i) global planarization and (ii) low defect and contamination level. The main challenge of cleaning is to remove the residual particles as well as the metallic contamination. In this paper, a modified post-CMP clean up—multi-chemicals spray cleaning process—is addressed in detail. This new process has been successfully applied to both oxide and tungsten CMP cleaning. The process provides comparable defect performance and excellent removal of metallic contamination to the scrubbing process which has been widely accepted in current post-CMP cleaning usage. The new clean up development strategy also contributes to their low cost of ownership (CoO) and good process flexibility as well as the minimizing cross-contamination. © 1998 Elsevier Science S.A.

Keywords: Chemical mechanical polishing; Post-CMP cleaning; Tungsten CMP; Multi-chemicals spray cleaning; Metallic contamination

1. Introduction

As device sizes are scaled down to sub-half-micron dimensions, planarization technology becomes increasingly important. Chemical mechanical planarization (CMP) is rapidly becoming a standard process in all fabs which multiple metal interconnect layers are required in their devices. CMP of dielectric (silicon oxide) films is widely accepted as the choice of planarization process for the technologies of dense topographical features in multilevel metal interconnect structure [1–4]. Additionally, the CMP of CVD tungsten films can be used for the formation of high aspect-ratio intermetal plugs and interconnect lines by a damascene process [5,6].

A major problem in the semiconductor industry today is the removal of residual slurry, particles and metallic contaminants from the wafer surface after the CMP polishing process. Many papers have been published on the topic of CMP [7], yet few literature exists on the topic of post-CMP clean up [8]. The need for cleaning is based on the fact that the surface environment of the wafer is changed by chemical-mechanical action—the CMP process. The presence of residual slurry introduces foreign particles, metallic contaminants

and chemicals typically undesirable for the remaining steps of chip fabrication. Ideally, post-CMP cleaning would remove all these foreign elements in a quick, repeatable fashion, without introducing further defect damage to the wafer surface. The generally desired requirements for an acceptable post-CMP cleaning included: (1) low surface defect level: <40 defects/wafer for >0.2 μm in size; (2) trace metals below transmission X-ray fluorescence (TXRF) detection limit, and (3) no change in surface roughness. During recent years, scrubbing wafer with soft brushes to clean polishing residues is the main choice in most post-CMP applications [9]. The effectiveness of scrubbing technique in removing surface defects has been demonstrated in Refs. [8,10]. However, issues of trace metallic contamination removal have been addressed in research works [11], which have not yet found their way into production worthy tools. Moreover, there are some drawbacks for scrubbing cleaning. Owing to the cylindrical polyvinyl alcohol (PVA) brushes directly contacting the wafer, wafer surface scratches and wafers' cross-contamination are possible.

There is a significant difference between the challenge of cleaning process for oxide CMP and tungsten (W) CMP. In the case of the W-CMP process, the low pH alumina-based slurry used to polish the tungsten film is more difficult to be

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cleaned by scrubber. In addition to removal of tungsten slurry residue, it also needs to be highly desirable to remove the trace metallic residue that is left on the oxide film. Most commercially available W-slurries use oxidants containing heavy metal ions, e.g. either $\text{Fe}(\text{NO}_3)_3$ or KIO_3 . In this paper, we introduce a modified multi-chemicals spray cleaning process for both after-oxide and W-CMP cleaning. The configuration of the cleaning processor is shown in Fig. 1. The spray processor system provides the function for automatic centrifugal spray cleaning with corrosive or caustic chemicals. It was first introduced by FSI in 1981 [12]. In a spray processor, a batch of post-CMP wafers contained in four cassettes are loaded into a turntable that rotates the wafers past a stationary spray post. Filtered acids and reagent solutions are applied into the chamber through a liquid feed system which includes pressurized spray, a mixing manifold, and nitrogen atomization. The spray is directed uniformly through the spray post at the wafers and the spent chemicals are drained continuously through the bottom of the bowl so that fresh chemicals always contact the wafers. This eliminates solution contamination and degradation problems possible with immersion techniques [13]. The spray processor performs the entire cleaning sequences, including all rinses and final drying steps, without moving the wafer from the equipment.

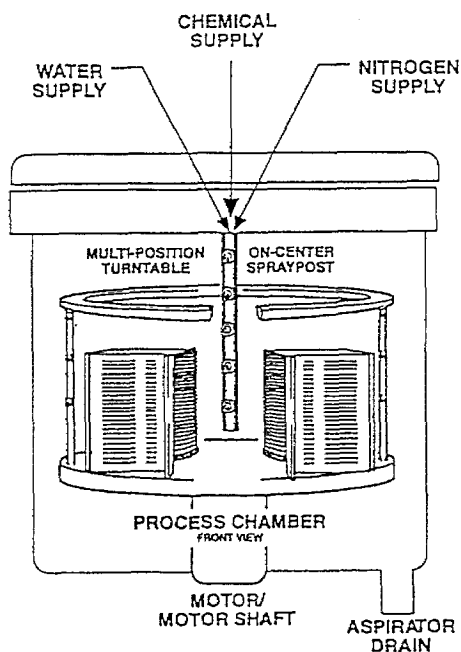


Fig. 1. The configuration of multi-chemicals spray cleaning processor.

2. Experiment

All the data presented in this paper were obtained from the 8" testing wafers. Blanket oxide, blanket W, and patterned wafers were used in this study. The blanket oxide test wafers were coated with 1000 Å of plasma deposited TEOS oxide (PETEOS). The blanket W test wafers were consisted of W-5000 Å/TiN-1000 Å/Ti-500 Å films stack on PETEOS substrate. For W-CMP studies on patterned wafers, test structures consisting of both contact features and inlaid line features were used. The data was typically collected from dense W plug array area with 0.4 μm in plug size and 1 μm in pitch.

The polishing process was performed on a Westech Model 472 polisher. The polishing pads were IC 1000/Suba-IV perforated pads made by Rodel. The KOH-based colloidal fumed silica slurry (SC-112) from Cabot was used for the oxide CMP. Two types of commercially available slurries, Cabot's W-A335/FE-10 $\text{Fe}(\text{NO}_3)_3$, oxidizing agent based slurry and Rodel QCTT1011 KIO_3 oxidizing agent based slurry, were used for W-CMP study. Both of the W-slurries contain fumed alumina dispersed as the abrasive particles. The modified multi-chemicals spray cleaner used in this study had a standard configuration from FSI MERCURY spray processor, but were modified to be chemically compatible with dilute acids such as NH_4OH , H_2O_2 , HF, HCl, and also DI water. All the chemicals can be heated before delivering to the chamber. Most of the cleaning recipes were modified and followed the procedure formulated by Kern and Puotineu at RCA, which hence are often referred to as the RCA method [14]. Table 1 lists the clean recipes used in this study.

The DSS-200 OnTrak post-CMP scrubber system was also used for comparison. The scrubber solution spray were used 0.5% NH_4OH and DI water. Each of the test wafers must be processed by cleaner within a short time after CMP polishing to avoid slurry drying. The performance after the cleaning process was examined for both defects and metallic contaminants on wafers. Oxide wafers' surface defects were measured by a Tencor 6420 light-scattering system, and tungsten wafers were measured by a KLA digital comparison system. The metal contamination was checked using a Rigaju-3700 TXRF and secondary ion mass spectroscopy (SIMS). Surface roughness was measured using atomic force microscopy (AFM). The oxide thickness measurements were taken on a Tencor FT-750, while tungsten films thickness were measured on a Tencor RS-75.

Table 1
RCA clean used in this study

Cleaning recipe	Solution	Temperature	Time
APM (Ammonia/Peroxide mix)	$\text{NH}_4\text{OH} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ 1:1:5	75–80°C	10 min
dilute HF dip	$\text{HF} + \text{H}_2\text{O}$ 1:50	25°C	10–25 s
HPM (Hydrochloric/Peroxide mix)	$\text{HCl} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ 1:1:6	75–80°C	10 min

3. Results

All the polished oxide and tungsten wafers were cleaned in the spray processor using different chemicals. The combined effects of APM, dilute HF dip and HPM were evaluated on the surface defects, metallic contamination and surface roughness.

3.1. Post-oxide CMP cleaning result

Most of the post-oxide CMP wafer surface in semiconductor manufacturing consists of planarized SiO₂ (typically with no other exposed material or topographical features), residual colloidal silica particles, and metallic ions penetration during CMP process. Therefore, the clean performance for blanket oxide wafers can really show the same results for the device wafers. In order to improve the particles removal efficiencies, the NH₄OH mixing ratios in APM have been evaluated. Fig. 2 shows the particle removal ratios for different cleaning

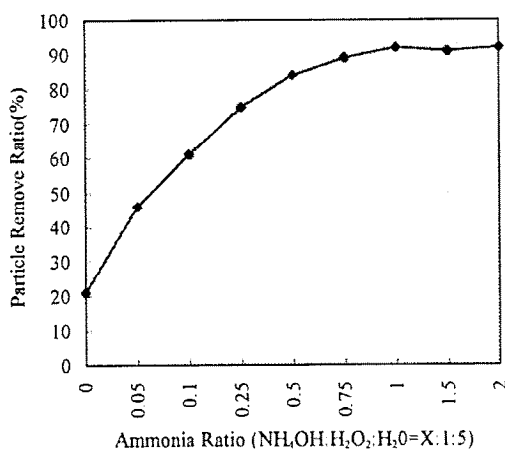


Fig. 2. The particle removal ratios for different cleaning NH₄OH ratios.

Table 2
The particle removal rate for modified clean recipes

Clean recipe modification	Particle removal rate
Standard APM process	92%
Adding liquid injection pressure	94%
Chemical pre-wetting time 5 s	95%
Adding liquid injection pressure + Chemical pre-wetting time 5 s	97%

NH₄OH ratios. From the result, the particles removal efficiency is very sensitive depending on the NH₄OH content ratio in APM. Also, in order to get the excellent particle removal rate, the cleaning recipe has been modified by increasing the chemicals liquid injection pressure and chemicals pre-wetting time. Table 2 shows the results for the modified clean recipes. Since the oxide surface is hydrophilic (wet with wafer), so more wetting time and higher physical pressure are believed to help the particles removal capability.

The combined effect for APM, dilute HF dip, and HPM was also evaluated. In order to eliminate the possibly poor surface roughness after HF dip, the different dilute HF dip times were also examined. Table 3 lists the results for different combined cleaning recipes.

According to the information in Table 3, the combined cleaning recipe for APM, dilute HF dip, and HPM exhibits a much lower level of metallic ions than that of the OnTrak scrubber cleaning. The new cleaning recipe provides a "clean" wafer surface which shows comparable defects and metallic ions performance as the wafer without CMP and cleaning process. The dilute HF dip 15 s is enough for the defect and metallic contamination removal, however, the HF dip 30 s will get more oxide loss and worse surface roughness, thus it is not recommended. The sequence of the clean recipe

Table 3
The clean effect for several combined cleaning

Clean recipe	Defect (>0.2 μm)	Oxide loss (Å)	Surface roughness by AFM (Å)	K	Na	Al	Ca	Fe	Cu
APM + HF dip 5 s	39	15	3.14	12.23	14.72	10.71	3.84	2.04	1.07
APM + HF dip 15 s	21	42	3.43	4.84	11.21	-	3.38	1.14	1.08
APM + HF dip 30 s	19	85	4.85	4.71	10.88	-	3.24	1.13	0.98
HF dip 15 s + APM	124	40	3.52	18.81	16.79	15.25	5.29	1.64	1.19
APM + HF dip 15 s + HPM	19	43	3.38	3.38	-	-	-	0.62	0.92
APM + HF dip 15 s + APM + HPM	11	45	3.47	3.22	-	-	-	-	1.01
Standard OnTrak scrubber	24	3	2.92	26.44	18.72	14.78	6.58	2.18	1.14
Blanket oxide wafer (No CMP and cleaning process)	10	-	2.84	-	-	-	3.03	1.25	0.95

The metal ion concentration measured by TXRF, the unit: E10 atom cm⁻². "-" indicates under detective limitation.

The detective limitation: K < 2.6 E10 atom cm⁻²; Na < 10E10 atom cm⁻²; Al < 4.3 E10 atom cm⁻¹; Ca < 1.8 E10 atom cm⁻²; Fe < 0.5 E10 atom cm⁻²; Cu < 0.5 E10 atom cm⁻².

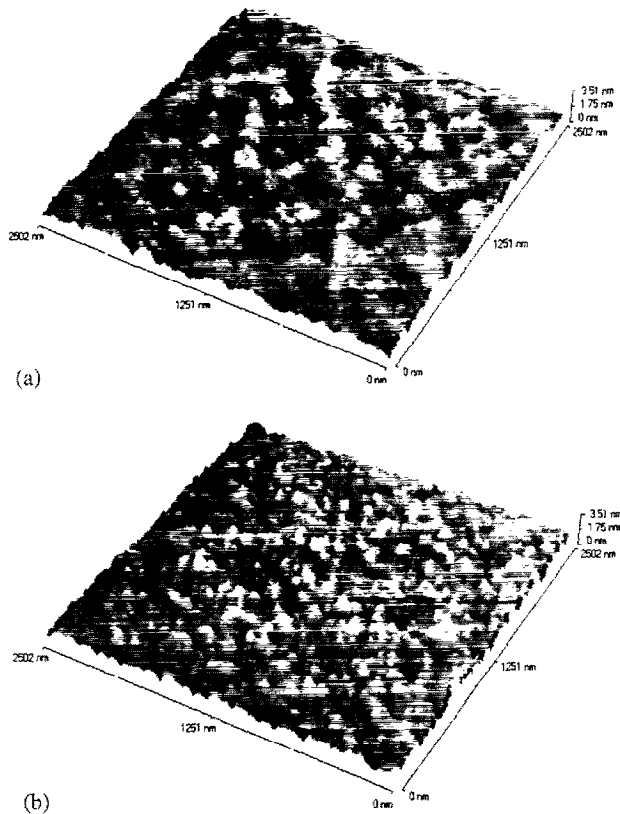


Fig. 3. Schematic diagram of the mechanical process involved in CMP.

is important; for this the “HF dip prior than APM” shows more worse defect level and metallic contamination than “APM prior than HF dip”. Figs. 3 and 4 show the comparison on AFM and SIMS analysis between the “APM + HF dip 15 s + HPM clean” and “OnTrak scrubber clean”. In order to eliminate the surface fluctuation for SIMS analysis, we have deposited 0.1 μm low temperature amorphous silicon film on the oxide surface with Applied P-5000 chambers before the SIMS measurements.

3.2. Post-tungsten cleaning results

W-CMP presents a very different substrate and set of conditions to the post-clean process. The wafer surface consists mainly of planar SiO_2 and a small percentage of tungsten features. These features are typically slightly recessed from the SiO_2 surface, and possibly dished rather than planar. Also, the residual abrasive particles are typically suspended Al_2O_3 (alumina) which may have different adhesion coefficients to each of the exposed ones. Therefore, the post W-CMP cleaning performance needs to examine the defect level, Al_2O_3 abrasive, as well as oxide recessed. Table 4 shows the defect level and the film thickness loss during different clean-up strategies. Fig. 5 shows the KLA defect mapping on wafers for the comparison of “APM + HF dip clean” and “scrubber clean”. In order to identify the distribution of defects, the SEM image of the same wafers over plug area are also shown

Table 4

The cleaning result for different post W-CMP (QCTT1011 slurry) clean-up

Clean recipe	Oxide loss (\AA)	W loss (\AA)	KLA defects
APM + HF dip 20 sec	43	62	24
APM + HF dip 60 sec	108	224	39
HF dip 20 sec + APM	41	58	286
OnTrak scrubber	<5	<5	891

in Fig. 6. From the above results, the “APM + HF dip” process show excellent removal for the residual slurry and particles, while the “scrubber clean” will remain residual slurry particles at the tungsten plug area (see Fig. 6(b)). It is believed that the adhesion coefficient between the Al_2O_3 abrasive and W-plug is very strong and cannot be removed by physically scrubbing only. However, the chemical clean for APM and HF etching can remove the slurry particles from the W surface.

A study of the morphology of a 0.4 μm W-plug structure was made by using AFM. The purpose of this experiment is to demonstrate the compatibility of the “AFM + HF dip” process with all of the materials in the W-plug structure. Fig. 7(a) shows a line scan through the plug after the “APM + HF dip 20 s” cleaning. Although an estimated 40 \AA of oxide and 65 \AA of tungsten was etched, the depth of the W-plug structure increased by approximately 25 \AA . The total recess of the plug, approximately 70 \AA below the plane of the surrounding oxide, is still tolerated for the subsequent processing step. The situation is different when 60 s HF dip is used. Fig. 7(b) shows the same plug after a “APM + HF dip 60 s” process. In this case, the plug structure was more severely attacked and a significant amount of W was removed. The plug material removal for the extended HF exposure (60 s) would not be tolerated. It is clear that the use of HF in post W-CMP cleaning must be properly controlled to avoid attacking the plug-structure. In order to evaluate the cleaning performance of the metallic contamination by TXRF after different W-slurry polishing, a comparison between the different cleanings are made on the non-pattern wafers. The wafers were polished until all the metal layers were removed. Consequently, the oxide layers were exposed to the slurry and then the following cleaning process. Table 5 shows the TXRF results for different slurries and cleaning.

From the results shown in Table 5, the “APM + HF dip” shows a much better metallic contamination removal than the traditional scrubber clean. According to the above study, a new multi-chemicals spray process for “APM + HF dip 20 s” is easily tolerated by the W-plug structure and provides good removal of the slurry particles and any residual metallic contamination in the surrounding oxide.

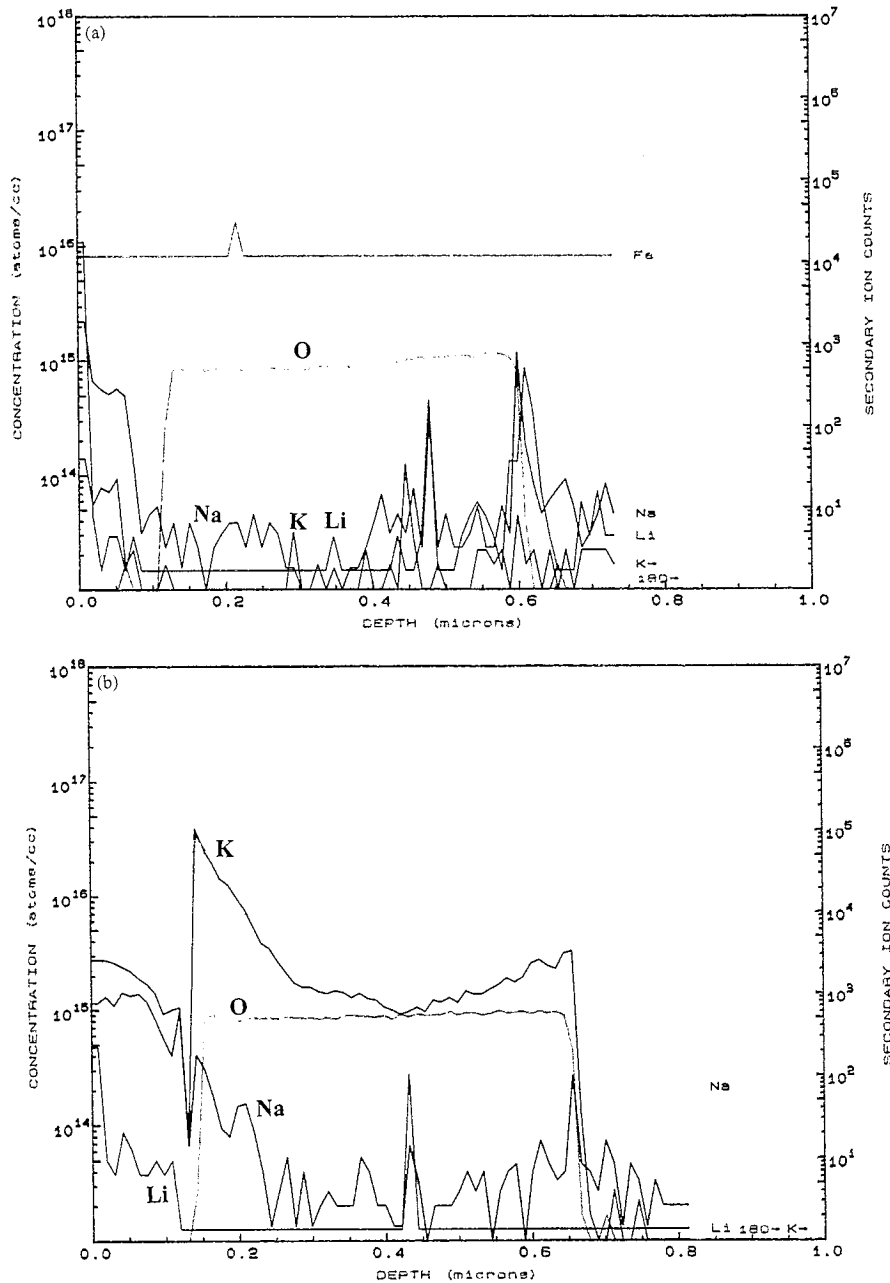


Fig. 4. (a) The SIMS analysis for (APM + HF dip 15 s + HPM) post-oxide CMP clean. (b) OnTrak scrubber post-oxide CMP clean.

4. Discussion

In trying to define the mechanisms behind the ability to clean post-CMP wafers, the concept of zeta potential has become a viable explanation. The enhanced cleaning ability of NH_4OH and H_2O_2 solution is believed to be explained by a strong relationship that exists between the pH and zeta potentials of these solutions and other materials present in the cleaning environment. A diagram depicting zeta potential versus pH for silica, alumina, and tungsten can be seen in Fig. 8 [15]. It is believed that when the zeta potential between the slurry particles and wafer surface are all the same sign (either positive or negative), it will be easier for the particles to be removed from the wafer surface due to the electrical

repulsive forces. Particularly, for the post W-CMP cleaning, which follows a low pH (typically within 2.7–4.5), alumina-based slurry CMP process, cleaning is more difficult because the zeta potentials between materials have different signs (the alumina particles of the slurry exist in a positive regime, in contrast with the rest of the wafer environment). The APM cleaning is thus important for the slurry particles removal which provides a high pH environment in order to change the zeta potentials from different signs to the same signs. Also, from Table 2, it has been proven that the increasing pressure liquid injection and chemical pre-wetting time can help to reduce particles settling during APM cleaning. It can be easily explained that high pressure spray helps to physically remove particles, but can reduce the availability for surface chemical

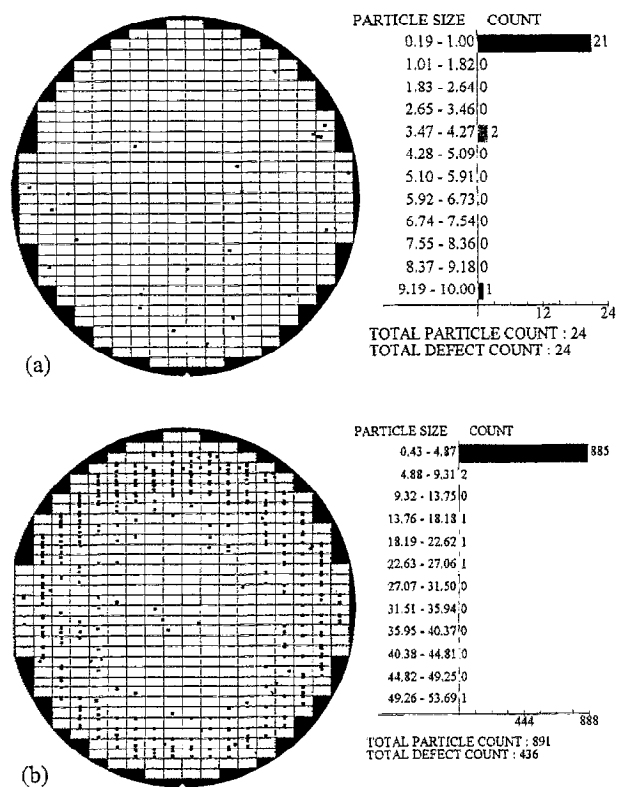


Fig. 5. KLA defects analysis for (a) (APM+HF dip 20 s) post-WCMP clean, and (b) scrubber post-WCMP clean.

reactions that are sometimes required for removal of particles. So the increasing pre-wetting time is necessary for excellent particle removal rate.

There is a clear advantage of etching a thin layer of oxide or tungsten with the dilute HF (approximately 40–60 Å in this study). Since the CMP slurry contains the KOH, $\text{Fe}(\text{NO}_3)_3$ or KIO_3 aqueous, it is possible for the penetration of the potassium and ferric ions into the wafer surface layer during CMP polishing. Also the oxide or tungsten films near the polishing surface are believed to be damaged during polishing. The metallic ions can be “trapped” in the damaged films and can be very difficult to remove with cleaning agents. Therefore, a light surface etching which carries off the contaminants is the only way for removal of the sub-surface contaminants. When the oxide or tungsten is removed by the dilute HF, the metal contamination and damage layer are also removed, resulting in a surface layer with very low metallic contamination and damage. There is a significant difference between the traditional RCA clean and post-CMP cleaning for the effect of changing the sequence of chemical cleaning steps. It has been widely accepted that a dilute HF etching prior to the APM cleaning can result in a very low metal and particle contaminants [14]. However, according to the results shown in Table 3 and Table 4, when the order of the dilute HF and APM steps are switched, particles and metal level are decreased by approximately a factor of four or five. It is believed that the challenge for post-CMP cleaning is to remove most of the residual slurry particles with the APM solution in the first step. Then, once the slurry particles have

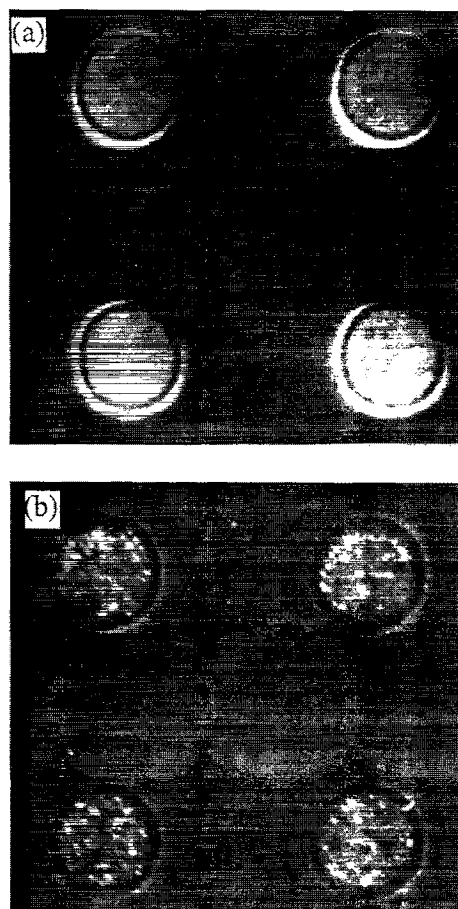


Fig. 6. SEM image defects analysis for (a) (APM+HF dip 20 s) post-WCMP clean, and (b) scrubber post-WCMP clean.

been removed, the dilute HF in the second step is able to etch the top 40–60 Å of oxide or tungsten, thereby removing the metallic contamination which has been incorporated in the surface and near surface region. Otherwise, if the HF dip is prior to the APM cleaning, the slurry particles cannot easily be removed during HF dip because the zeta potential between the materials are different signs. The surface region under the slurry particles should not be etched and metallic contamination can be difficult to remove with the following cleaning agents.

Table 3 also shows the cleaning effect for the HPM ($\text{HCl} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$). From the result, the HPM shows excellent capability for the removal of sodium, alumina, ferric and calcium metal ions for post-CMP cleaning. The above metallic contamination is not only associated with slurry particles, it is also possibly presented in the liquid parts of the polishing slurry or may come from polishing equipment, pads and pad conditioning tools. These type of metal ions can be easily removed by the HPM cleaning. This cleaning method for improving the solubility is the formation of soluble complexes. Thus, the Cl^- anion used in the solution is important, since it may contribute to complex formation. The metal ions act as the electron acceptor and the Cl^- anion acts as the electron donor in the formation of an inorganic soluble complex. However, the HPM cleaning is not recommended for

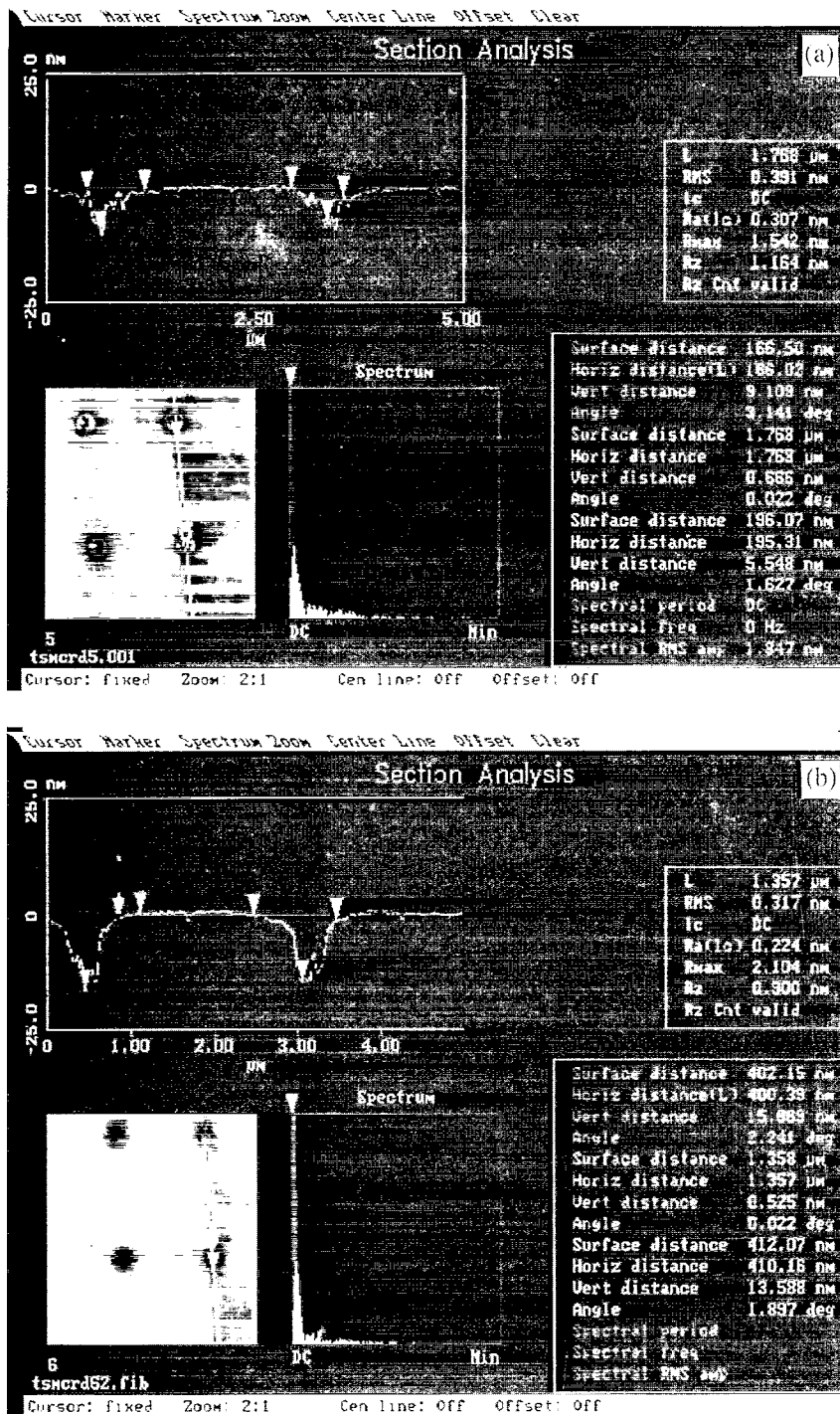


Fig. 7. AFM line scan through the plug for (a) (APM + HF dip 20 s) post-WCMP clean, and (b) (APM + HF dip 60 s) post-WCMP clean.

Table 5
TXRF results for post W-CMP cleaning

Clean recipe	Slurry	K	NA	Al	Ca	Fe	Cu
APM + HF dip 20 s	Rodel KIO ₃ -based	22.7	14.5	58.3	10.7	1.54	1.89
Scrubber clean	Rodel KIO ₃ -based	156	63.8	1418	562	28	13
APM + HF dip 20 s	Cabot Fe(NO ₃) ₃ -based	14.8	11.52	87.2	16.5	5.4	1.57
Scrubber clean	Cabot Fe(NO ₃) ₃ -based	28.3	88.4	2400	221	865	19

Unit: E10 atom cm⁻².

Table 6
The manufacturing concern for spray and scrubber clean-up strategy

Item	Spray processor	Scrubbing system
Throughput (wafers/h)	128	61
Cost of Ownership (\$/wafer)	x	1.65x
Process flexibility	Both for oxide and W-CMP	Need to be separated
Water usage	Need DI water when processing only (low water consumption)	Continue using DI water—4 gallons per min (very high water consumption)

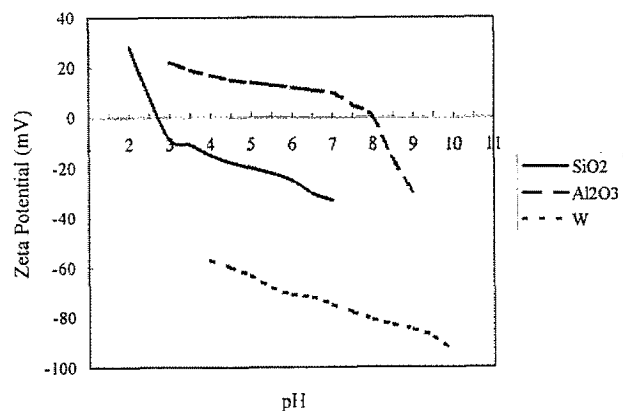


Fig. 8. Diagram depicting zeta potential vs. pH for silica, alumina, and tungsten.

post W-CMP cleaning due to the concern of possible metal corrosion issue from HCl chemicals. So the HPM cleaning is only an optional step for the post oxide CMP cleaning such as inter-poly-metal dielectric (ILD) polishing process in order to improve device performance as well as reliability issue.

Except the excellent final defect level and the level of residual metallic contamination, the post-CMP clean-up strategy for the multi-chemicals spray cleaning also provides some benefits for the manufacturing concern. In comparison with the traditional scrubbing process, the new cleaning method shows higher throughput, lower cost of ownership (CoO) and process flexibility. The spray processor can be used for both post-oxide CMP and W-CMP cleaning in the same machine by using the continuous fresh chemicals for different clean recipes. However, the scrubber system allows the risk for the wafers cross-contamination issue when processing two types of oxide and tungsten cleaning with the same PVA brush. Table 6 lists the comparison of two clean-up strategies for the manufacturing concern.

5. Conclusions

Wafers after CMP polishing are contaminated by particles and metallic ions. Some of contamination is metallic impurities in slurry, the other contamination may come from the polishing system. A new post-CMP clean-up strategy for both oxide and W-CMP cleaning has been developed by using the

modified multi-chemicals spray cleaner. This process provides a low level of trace metallic contamination and comparable defect levels than the traditional scrubbing process. Also, the new clean process shows high throughput, low cost of ownership and good process flexibility. Although all the mechanisms behind post-CMP cleaning are not yet fully understood, it is clear that the mechanical, chemical, and electrical effects will be important in optimizing post-CMP cleaning. Significant improvements have already been realized in manufacturing environments.

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