

# Advanced Front-End-of-the-Line Cleaning

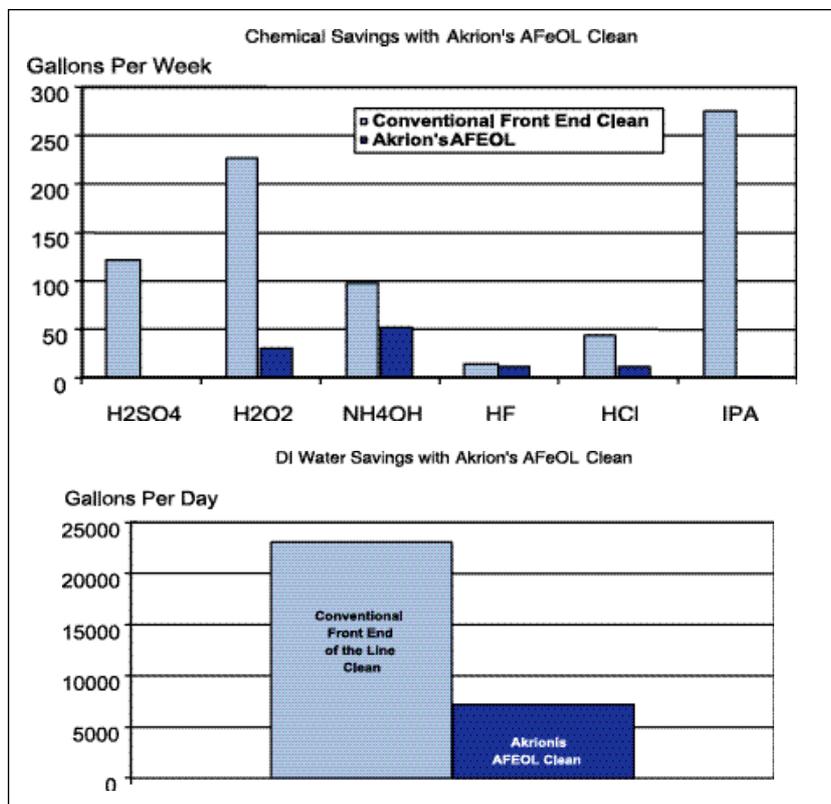
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## ABSTRACT

**T**he control of microcontamination on silicon surfaces prior to oxidation is becoming increasingly important. Tighter control of surface microcontamination than can be achieved with conventional processes is required for future devices. There is also interest in reducing cost of ownership and chemical waste without affecting yield or device performance. An advanced front-end-of-the-line cleaning tool/process, which has reduced the size of the equipment by 40%, reduced the overall deionised water consumption by 60% and reduced chemical consumption by 85%, is described. Results for particle removal efficiency, metal removal efficiency, surface roughness, film removal and electrical data are described.

## INTRODUCTION

With the continued shrinking of design rules, the control of microcontamination on silicon surfaces prior to the oxidation process has recently received increasing attention [1–3]. In particular, the characteristics of the interface between the oxide and the silicon have a direct impact on the oxide performance, and efficient cleaning steps to remove various microcontaminants (such as particles, metallic impurities and organic residue as well as native oxide) are essential to obtain high-quality oxide [4]. Traditionally, most pre-diffusion cleaning processes have been performed with either an HF-last procedure (APM/(HPM)/DHF) or a standard SC2-last procedure (DHF/APM/HPM) (where “DHF” is an HF–H<sub>2</sub>O mixture, “APM” is an NH<sub>4</sub>OH–H<sub>2</sub>O<sub>2</sub>–H<sub>2</sub>O mixture and “HPM” is an HCl–H<sub>2</sub>O<sub>2</sub>–H<sub>2</sub>O mixture). Although these conventional cleaning processes have demonstrated robust and stable process capability in recent years, much tighter control of surface microcontamination is required for future smaller and more complex devices. The main issue associated with the HF-last procedure is contamination by small particles, as hydrophobic surfaces are known to promote particle contamination. In the SC2-last cleaning process, the unreliable chemically grown oxide has a negative impact on the electrical performance of the thin oxide. The chemical oxide formed during pre-diffusion cleaning is a significant part of the total thickness of sub-30 Å gate dielectrics, but new concerns about the wet-chemically-grown oxide have been raised. An additional SPM cleaning (“SPM” is an H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> mixture) is an effective process for removing heavy organic moieties; however, post-piranha residue adheres tenaciously to the wafer surface, contributing to process-induced microdefect growth during the follow-up oxidation process [5].



In addition to these concerns, there has been much activity focused on reducing cost of ownership in cleaning processes and chemical waste without affecting yield or device performance. Traditional solutions have included automated and manual wet stations exceeding

Figure 1  
Chemical and DI water savings with AFeOL cleaning

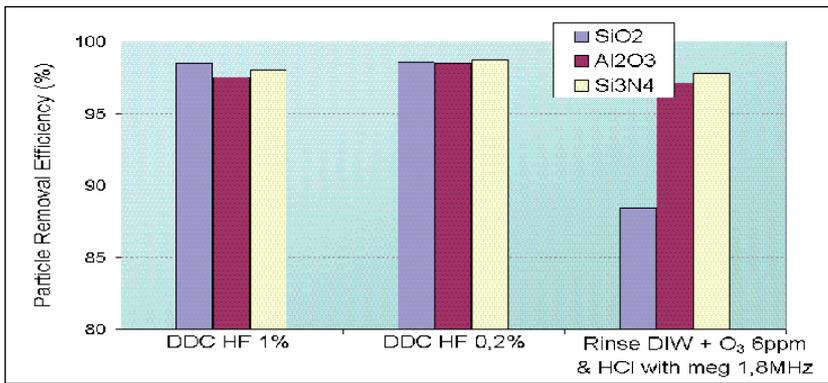
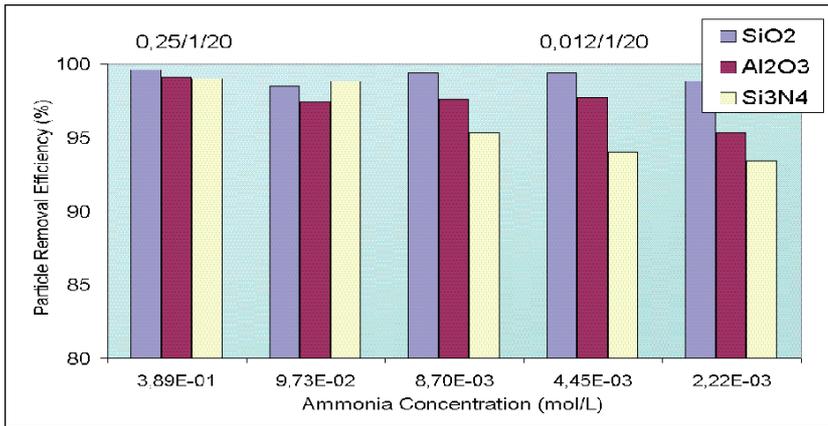


Figure 2 (top)  
Dependence of APM particle removal efficiency on NH<sub>4</sub>OH concentration

Figure 3 (above)  
Particle removal efficiency of HF-HCl-DI water solution

8m in length and consuming high volumes of chemicals and deionised (DI) water. While the process results associated with these large wet-process tools are robust, they are fast approaching the limit in device processing for defects and ionic contamination.

The new age of semiconductor manufacturing with smaller design rules and contamination-sensitive features requires new methods of wet cleaning. Improvements in process performance and cost-effectiveness will be essential, for which modified or alternative chemistries such

as ozonated DI water (Akrion's DIO<sub>3</sub><sup>TM</sup>) [6, 7] and HF/HCl mixtures [1, 2] are being proposed and used with varying degrees of success.

Akrion has developed an advanced front-end-of-the-line cleaning tool/process (AFeOL), which has broken the traditional barriers and reduced the size of the equipment by 40%, reduced the overall DI water consumption by 60% and reduced chemical consumption by 85%. Figure 1 shows the difference between conventional pre-diffusion/pre-gate cleaning and AFeOL cleaning.

### PROCESS DETAILS

Akrion's AFeOL clean is a robust cleaning process, which eliminates five of the process steps associated with the traditional "front-end" cleaning (see Table 1).

In step 1 of the process, ambient ozonated DI water (DIO<sub>3</sub>, 5–50 ppm) is used in place of high-temperature SPM to remove organic contamination and transition metals. To ensure the proper ozone concentration in the bath, a point-of-use in-line concentration sensor is used. In addition to the obvious benefit of eliminating sulfuric acid, a DI water rinsing step is not required after DIO<sub>3</sub> treatment; this not only eliminates the need for sulfuric acid but also reduces the use/disposal of DI water by as much as 90 gallons (per 50 wafers).

In step 2, a transitional APM process is utilised. The APM process takes advantage of Akrion's 1600 watt Turbo Phaser Megasonic and its patented ICE-1<sup>TM</sup> concentration control. The ICE concentration control allows the user to use the same bath for 24–72 hours, depending upon the process condition and application. ICE takes the guesswork out of the chemical concentration in the bath. After the SC1 step, the next step is a traditional DI water rinse (step 3).

Step 4 combines diluted HF and HCl. This bath removes any native oxide, but the HCl injection also performs an ionic removal and neutralisation process. Another benefit of the HCl is that it changes the zeta potential of the bath, thus providing effective particle removal.

Step 5 is a traditional DI water rinse, but the system can be programmed to inject ozone into the rinse bath

**TABLE 1. COMPARISON OF TRADITIONAL PRE-DIFFUSION AND AFeOL CLEANING PROCESS SEQUENCES**

Process Step	Traditional Process (Bath Life)	Akrion's FeOL Clean (Bath Life)
Step 1	SPM - H <sub>2</sub> SO <sub>4</sub> :H <sub>2</sub> O <sub>2</sub> (24 hrs.)	DIO <sub>3</sub> (96 hrs.)
Step 2	Hot Quick Dump Rinse	SC1 Meg – DI:NH <sub>4</sub> OH:H <sub>2</sub> O <sub>2</sub> (24 hrs.)
Step 3	DHF – 50:1 (72 hrs.)	Quick Dump Rinse
Step 4	Overflow Rinse	DHF/HCL: 100:1:1 (96 hrs.)
Step 5	SC1 Meg – DI:NH <sub>4</sub> OH:H <sub>2</sub> O <sub>2</sub> (24 hrs.)	Overflow Rinse (*Ozone Injection)
Step 6	Quick Dump Rinse	Akrion's LuCID <sup>TM</sup> Dry
Step 7	SC2 – DI:HCl: H <sub>2</sub> O <sub>2</sub> (12 hrs.)	
Step 8	Quick Dump Rinse	
Step 9	Final Rinse	
Step 10	Dry	
Throughput:	180 wph	220 wph

\* – Ozone Injection is required for Hydrophilic Process

to convert the hydrophobic wafer surface to hydrophilic. The major benefit is that in the traditional pre-diffusion clean, the hydrophobic surface is converted to hydrophilic using the  $H_2O_2$  from the APM and HPM process steps. This chemical oxide is typically high in ionic contamination; however, the  $DIO_3$  treatment grows an oxide that is free from ionic impurities.

Step 6 is a wafer-drying step using Aktron's LuCID (low-consumption IPA dryer), which utilises a patented point-of-use DI water filter and patented isopropyl alcohol (IPA)/nitrogen drying process. This dryer uses approximately 6–8 ml of IPA per fifty 200 mm wafers (compared with 400–550 ml of IPA in ordinary vapour dryers).

## PROCESS RESULT S

### Particle removal efficiency

APM chemistry with application of megasonics is a major contributor to the removal of particles on the wafer surface in this cleaning process, and, as shown in Figure 2, variation of the  $NH_4OH$  concentration in the APM does not strongly influence the particle removal ability. In fact, in concentrated solutions, the acoustic energy is absorbed and reflected by numerous fine bubbles during wafer processing; therefore, the particle removal mechanism relies on surface oxidation and etching. In dilute solutions, acoustic activation on the wafer surface is of prime importance for particle removal. For nitride particles, the efficiency drops only when the pH falls below 8. However, with diluted APM without application of megasonics, the particle removal efficiency drops significantly (to under 50%).

Particle readhesion after HF–HCl–DI water treatment has not been significantly observed, because of the control of the zeta potential between the hydrophobic silicon surface and the particles. In addition, the use of a high-frequency megasonic module during the subsequent rinse step shows excellent particle removal efficiency (Figure 3). The HF concentration reduction has a beneficial impact in minimising particle readhesion on the silicon surface. We can explain this phenomenon by the previously published Holy Grail effect [8], in which a higher density of etched species in the boundary layer on the wafer surface could significantly contribute to higher levels of particle readhesion. Figure 4 shows the number of added particles on hydrophobic Si surfaces as a function of the HF concentration in an HF–HCl–DI water mixture.

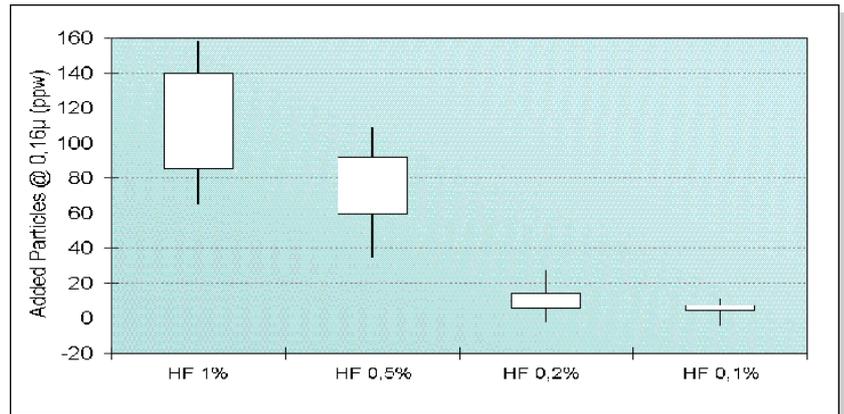
### Metal removal efficiency

In a traditional process, the metal removal mechanism is a complex reaction among ionic metals, reactive oxygen from  $H_2O_2$ , and HCl in higher-temperature HPM. However, in the AFeOL cleaning process, the ionic metal can be removed by two combined mechanisms:

(1) reaction between ionic metal and HCl to produce a metal halide

(2) the etching away of the chemically grown (from the previous APM step) oxide layer by HF

The advantage of the use of the HF–HCl–DI water mixture is not only reduction of the chemical cost by either eliminating  $H_2O_2$  or diluting the process chemistry, but also avoidance of high-temperature processes. After the HF–HCl–H<sub>2</sub>O treatment, the extra treatment with HCl–DI water during the rinse step makes sure that there is no extra metallic contamination on the silicon surface before regrowth of a high-quality metal-free passivation layer. Figure 5 shows the metal removal efficiency as a



function of the cleaning process, as measured by VPD-ICP mass spectroscopy.

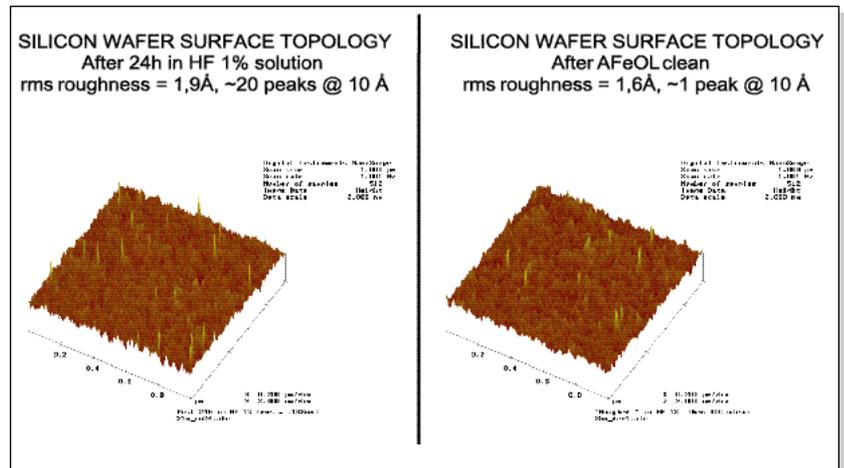
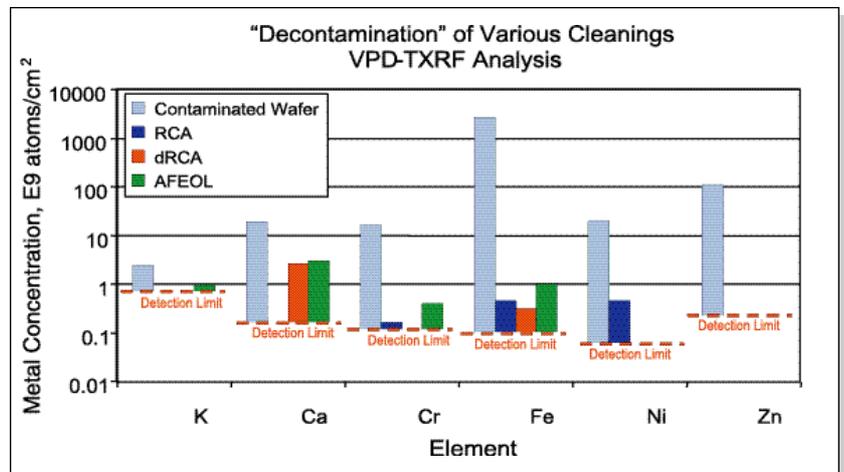
Figure 4  
Added particles on hydrophobic Si surface for various HF concentrations (Holy Grail effect)

### Surface roughness

The surface roughness generation mechanism is associated with both the oxidising reaction on the silicon surface caused by a strong oxidant such as  $H_2O_2$ , and the molecular reaction (so-called surface etching) between OH and the oxide film generated after the oxidation. Typically, the dominant factors that generate larger surface roughness are the process temperature and the concentration of  $NH_4OH$  in the APM solution. Therefore, the more dilute the chemistry and the lower the temperature applied to the process wafer, the less surface roughness we can expect. Figure 6 shows the difference in surface roughness between the traditional process and the AFeOL process.

Figure 5 (below)  
Metal removal efficiency as a function of cleaning process, measured by VPD-ICP mass spectroscopy

Figure 6 (bottom)  
Silicon surface roughness after each type of cleaning process



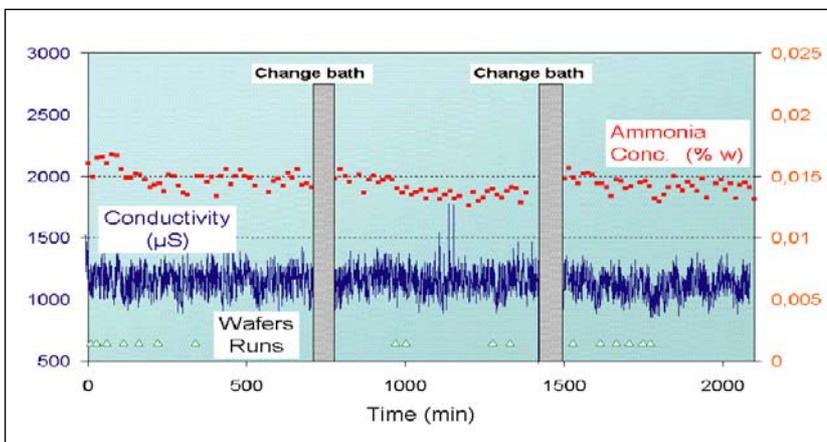
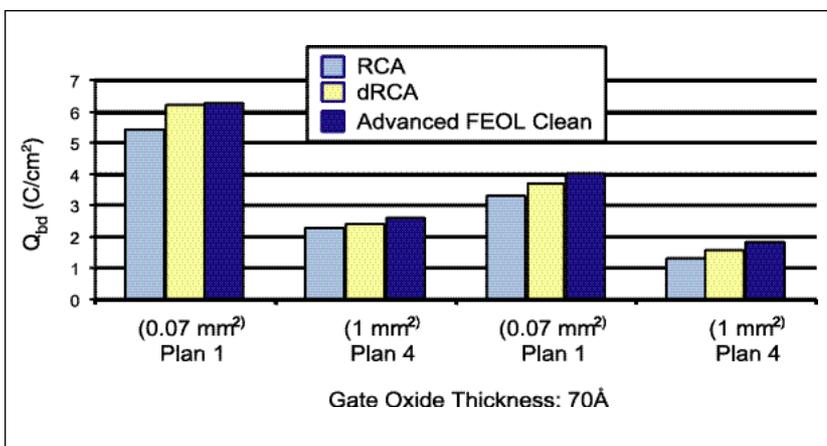
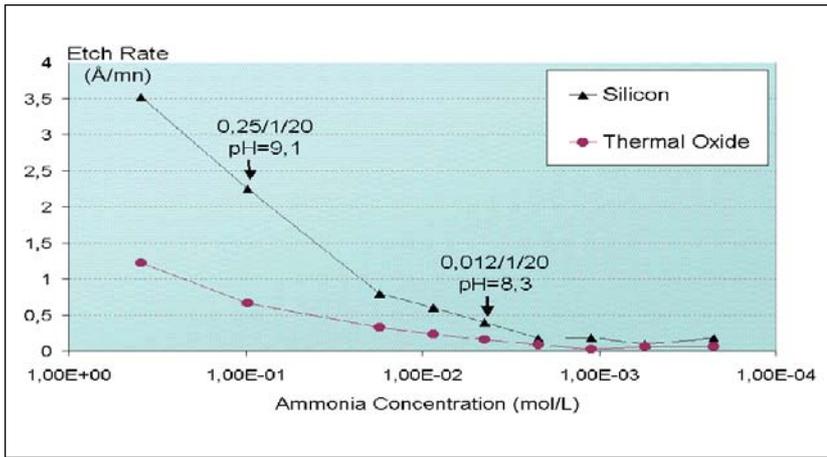


Figure 7 (top)  
Dependence of APM etch rate  
on  $\text{NH}_4\text{OH}$  concentration

Figure 8 (above middle)  
 $Q_{bd}$  distribution of 7 nm gate  
oxide structures

Figure 9 (above bottom)  
APM ammonia concentration  
control

### Film removal

In a pre-diffusion cleaning process, there are two parameters that control film removal ability. One is the concentration of the  $\text{NH}_4\text{OH}$  (in the APM solution) and of the HF (in the DHF solution); the other is the temperature of the process chemicals. In particular, minimising film removal ability with decent etch rate uniformity becomes important in various unit process such as pre-cleaning for spacer deposition, pre-cleaning for gate oxidation (including multi-gate oxidation) and pre-cleaning for contact fill processes. As expected, and as shown in Figure 7, when the ammonia concentration is decreased, the APM etch rate decreases on both silicon and thermal-oxide surfaces. As a result, we were able to reduce the Si and

$\text{SiO}_2$  consumed by factors of 5.5 and 4, respectively, as the composition of the APM solution was changed from 0.25/1/20 to 0.012/1/20.

When HF chemistry is used, the target with ultra-dilute HF-HCl-DI water (0.2/1/100) is 12 Å/minute with a one minute process. This etch rate can remove any native oxide as well as the chemically grown oxide on the silicon surface. Further dilution of the DHF chemistry does not change the total silicon consumption.

### Electrical data

A comparative electrical test on a 7 nm gate oxide structure was performed with a traditional RCA pre-diffusion cleaning technique, a diluted RCA solution, a previously published DDC cleaning technique and the AFeOL cleaning technique, before gate oxidation. The cumulative failures obtained from charge-to-breakdown measurements are shown in Figure 8. There is no significant variation among four different  $Q_{bd}$  distribution splits.

### Concentration control

Since the concentration of  $\text{NH}_4\text{OH}$  in the APM solution is a dominant factor in determining the film removal capability, the surface roughness of the silicon and the particle removal ability, the  $\text{NH}_4\text{OH}$  concentration needs to be tightly controlled. The parameters of the ICE conductivity control on Akrion's GAMA™ system were optimised by use of an in-line monitoring system with an ammonia ion-specific electrode and an oxidant reduction probe. The ability to properly control this low ammonia concentration is clearly demonstrated in Figure 9.

### RECOMMENDED PROCESS

On the assumption of an advanced gate oxidation process which typically uses a thickness of less than 40 Å, the following is the recommended process:

5 min  $\text{DIO}_3$  process (5–10 ppm of ozone) at ambient temperature to remove metallic and organic impurities by oxidation reaction.

10 min APM (0.12/1/20  $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{DI}$  water) process with a 1600 W Akrion Turbo Phaser Megasonic at 50°C to remove particles and extra-light organics.

5 min hot DI water rinse at 50 °C to rinse the residual APM from the wafer surface.

1 min HF-HCl-DI water (0.2/1/200) treatment at ambient temperature to remove chemically grown oxide and to prevent particle adhesion during/after cleaning process.

10 min  $\text{DIO}_3$  process (5–10 ppm of ozone) at ambient temperature to convert wafer surface from hydrophobic to hydrophilic.

8.5 min dry with an Akrion LuCID dryer to dry the wafers.

### CONCLUSION

The AFeOL process/tool combines the benefits of unique, patented technology to dramatically reduce the consumption of DI water and chemicals while providing the advanced process results needed for the next generation of integrated devices. The major accomplishments of this development are

- (1) eliminating high-temperature and environmentally unfriendly SPM processes
- (2) minimising both Si and  $\text{SiO}_2$  consumption during the cleaning process
- (3) removing native oxide with a low particle level with an HF-HCl- $\text{H}_2\text{O}$  mixture

(4) growing stable ozone-induced oxide on a hydrophobic Si surface

(5) lowering cost of ownership by application of ultradilute chemistry, while increasing throughput as well as reducing equipment footprint.

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