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CLEANING OPTIMIZATION FOR REDUCED CHEMICAL USAGE*

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The use of dilute SC-1 (NH_4OH:H_2O_2:H_2O) chemistry cleaning processes for particle removal from silicon surfaces has been investigated. Dilute chemistries can be highly effective, especially when high-frequency acoustic energy (megasonics) is applied. The high particle removal efficacy of the dilute chemistry processes presumably arises due to increased double layer effects caused by reduced ionic strength. Dilute chemistry SC-1 solutions exhibit somewhat reduced efficacy for removal of certain light organics; however, when dilute SC-1 is used along with other pre-gate cleaning steps (*e.g.*, HF, SC-2, and piranha), then the overall cleaning sequence is quite effective. In addition to providing robust cleaning processes, dilute chemistries also result in significantly lower chemical and rinse water usage. Waste water treatment requirements are also lessened when dilute chemistry cleaning solutions are employed.

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INTRODUCTION

The cleaning chemistries which are typically employed throughout integrated circuit fabrication have been in use for many years. Although the various cleaning chemistries are known to be effective for current generation integrated circuit design rules, the cleaning mechanisms and performance limits of these chemistries are still poorly understood. Through careful process optimization and understanding of cleaning mechanisms, these chemistries can often be modified to maintain or improve cleaning efficacy while reducing chemical usage [1,2].

The most common cleaning chemistries include aqueous oxidizing solutions used for the removal of heavy organic contamination, transition metals contamination, and particulate contamination. Mixtures of sulfuric acid and a strong oxidizer such as hydrogen peroxide are commonly used for the removal of high molecular weight organics (*e.g.*, ashed photoresist). Hydrochloric acid, typically combined with hydrogen peroxide (commonly

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DISCLAIMER

known as the SC-2 chemistry) is often used for the removal of transition metal species. Ammonium hydroxide mixed with hydrogen peroxide (commonly known as the SC-1 chemistry), is typically used for particle removal, often with applied high-frequency acoustic energy (megasonics).

In recent years, a substantial effort has been focused on optimizing the SC-1 and SC-2 chemistries for process performance. It has been shown that these chemistries may be substantially diluted, while still maintaining high cleaning efficacies. Optimization of the SC-2 clean has been reported elsewhere in the literature [3,4], and hence will not be discussed here. This paper will discuss the optimization of the SC-1 clean to minimize particle and organic contamination, environmental impact, and cost of ownership. Dilute SC1 cleans are effective in removing particles as long as sufficient megasonic power is applied. This reduces cost of ownership and environmental impact by minimizing chemical usage, rinse water usage, and waste treatment. Removal of certain light organics is effective provided that the diluted SC-1 step is used along with other steps as part of an overall pre-gate cleaning sequence.

EXPERIMENTAL

A series of experiments were performed to assess the process capabilities of dilute SC-1 chemistry cleaning. These experiments and results may be organized into three classifications: particle removal studies, organic contamination removal studies, and environmental implications.

A. Particle Removal Studies

To establish boundary conditions for the experimental matrix, the traditional chemical concentration of the SC-1 clean (1 part by volume NH_4OH, 1 part by volume H_2O_2, 5 parts H_2O) was the upper concentration limit. The dilute cleaning chemistry regime, including the effects of megasonic power and process temperature, was investigated using a design of experiments approach. The contamination challenge for these experiments was silicon nitride particles, deposited from an aerosol in a size range from 0.11 μm (metrology lower detection limit) to 0.30 μm. The wafers for these experiments were 150 mm Si<100>, pre-cleaned in a dilute (1:10:130) SC-1 chemistry to establish a constant surface condition. A Tencor Surfscan 6200® was used for particle metrology before and after both the particle deposition step and the particle removal clean. A screening experiment was first performed to determine the main effects for particle removal. An empirical response surface matrix was then evaluated to determine optimal conditions for particle removal.

Open circuit potential (OCP) and haze measurements were also performed to assess surface modification effects such as passivation and etching during exposure to SC-1 chemistry. Open circuit measurements have been discussed elsewhere [5], and will not be discussed in detail here.

Optical haze was measured using the haze channel on the Surfscan 6200. Haze can be defined as the ratio of light scattered from the surface to the light illuminating the surface (*i.e.*, optical noise). When silicon is exposed to an alkaline medium, the Si{100} plane is preferentially etched due to the lower packing density. The preferential etching results in a rough, facetted surface. This increased surface roughness increases optical noise [6], and thus attack of the silicon surface can be deduced from increased haze values.

B. Organic Contamination Removal Studies

Designed experiments were performed to evaluate diluted chemistry SC-1 with applied megasonics for sub 0.20 µm particle removal. However, because the SC-1 is an oxidizing chemistry, this solution attacks low molecular weight organic contamination as well as aiding particulate matter removal. This is particularly important because organic contamination, such as dioctyl phthalate (DOP), has been found to affect gate dielectric breakdown [7]. Experiments were preformed to ensure that dilution of SC-1 would not detrimentally affect removal of light organics.

Hexamethyldisilizane (HMDS) was the first organic contaminant chosen for these studies because it is commonly used in semiconductor fabs as an adhesion promoter in photolithography operations, and it can be deposited in a controlled manner via vapor-phase exposure. DOP, a commonly used plasticizer, was also used as an organic contamination challenge because it adheres less tenaciously to hydrophilic silicon surfaces than does HMDS, it too is a common airborne molecular contaminant in semiconductor facilities, and it is known to effect device electrical performance. After doping both hydrophilic and hydrophobic silicon wafers with either HMDS or DOP, wafers were processed through various dilutions of the SC-1 clean. Residual HMDS or DOP was measured by time of flight secondary ion mass spectrometry (TOF-SIMS). Isotopically labelled DOP was used to mitigate the interference effects of normal environmental contamination. HMDS has a unique fragmentation pattern in TOF-SIMS that obviates the need for an isotopically labelled tracer. The fragmentation ion used to identify HMDS was mass 73, $Si(CH_3)_3^+$. For the deuterated DOP, the fragmentation ion that was used was mass 153, $C_6D_4(CO)_2OH^+$. To normalize the data, the measured peak intensity for each of these species was ratioed to the $^{28}Si^+$ intensity.

C. Environmental Implications

The first ancillary benefit of using a diluted chemistry clean is the reduction in chemical usage. Calculations may be easily performed to determine the amount of chemical savings obtained by dilution of chemical process baths. Chemicals used in waste water treatment may also be reduced by reducing the amount of chemicals that need to be treated by the waste treatment facility. However, since most of the chemical effluent from production semiconductor fabs is acidic, waste water treatment savings from dilute SC-1 chemistries (which are basic) are negligible if the acidic and basic waste streams are treated together.

The other primary environmental benefit of dilute chemistry cleaning is the reduction in water used for wafer rinsing. Wafers are typically rinsed until the rinse water effluent reaches a predetermined resistivity. The time required to reach the desired resistivity was measured following SC-1 chemistries of various concentrations. Simple cascade overflow rinsing was used with a full, standard pitch, 150 mm wafer cassette. The target rinse water resistivity for these experiments was 15 MΩ-cm.

RESULTS AND DISCUSSION

A. Particle Removal Studies

The SC-1 chemistry ($NH_4OH:H_2O_2:H_2O$) performs well with respect to particle removal even when the concentration of both ammonium hydroxide and hydrogen peroxide are substantially reduced, provided sufficient megasonic power is applied. Contour plots of silicon nitride particle removal efficiency using chemical ratios of r=1 and r=0.01, where r is defined as the volume ratio of NH_4OH to H_2O_2, are shown in Figures 1 and 2. Inclusive in the plot of Figure 1 would be the traditional concentration chemistry, 1:1:5 (ratio of $NH_4OH:H_2O_2:H_2O$); chemistries as dilute as 1:100:6900 are included in Figure 2. A quadratic megasonic power response can be seen, as well as a large region where effective cleaning is obtained for both concentration regimes. The clean appears to be quite robust, with a large process window where effective particle removal is obtained. It is apparent from these data that reducing chemical concentration does not necessarily have a deliterious effect on particle removal. Indeed, electrostatic affects in the alkaline SC-1 most likely play an important role in achieving effective particle removal, and these electrostatic effects may be enhanced in dilute chemistries. Dilute chemistries possess reduced ionic strength, and as ionic strength is reduced, the double layer thickness is increased, thus repulsion is enhanced through zeta potential interactions [8].

The role of H_2O_2 in SC-1 particle removal is generally accepted to be reduction in surface roughness caused by preferential alkaline etching of the Si{100} plane. However, when H_2O_2 is eliminated from the dilute NH_4OH cleaning chemistry, no significant difference in particle removal efficacy is observed, as shown in Figure 3 (these data were obtained without applied megasonic energy). The H_2O_2 does not appear to play an active role in particle removal. Nor did the omission of H_2O_2 cause a measureable increase in optical haze on wafers which possess a native oxide, as shown in Figure 4. However, hydrophobic wafers which precleaned in dilute hydrofluoric acid, and therefore do not possess a thin chemical oxide, exhibited substantial increases in haze when processed through dilute aqueous ammonium hydroxide. Haze values were found to increase by as much as 3 ppm on hydrophobic wafers, compared to essentially immeasurable haze deltas (ppb range) for the hydrophilic samples. These results suggest that a thin chemical or native oxide is sufficient to protect the silicon surface from alkaline attack in highly diluted ammonium hydroxide. Since cleaning efficiencies appear insensitive to the presence of hydrogen peroxide when sufficiently dilute aqueous ammonia is used, these data also indicate that surface etching is not requisite to effective particle removal. These cleans need not be tailored to achieve a certain etch rate in order to be effective for particle removal.

B. Organic Contamination Removal Studies

In the first set of experiments using HMDS as the contaminant challenge, the HMDS was found to adhere more strongly to hydrophilic silicon than to a hydrophobic silicon surface. This is due, presumably, to a reaction of the amine nitrogen of HMDS with the hydroxyl groups of a hydrophilic surface (-OH terminated). This can be seen in Figure 5. The "as deposited" data of Figure 5 are for wafers which were stored in a photolithography bay of the Sandia microelectronics laboratory for one week. This is the method used to prepare the organic contamination challenge, and these data were included as a control group. All other wafers were subjected to various cleans, and the resulting residual contamination levels (normalized to the $^{28}Si^{+}$ peak) are presented. The "Fab Clean" data are for wafers which received a full pre-gate cleaning sequence, including HF (1:15), piranha (5:1), SC-1 (1:4:64), and SC-2 (1:1:10). The remaining groups of Figure 5 received dilute SC-1 or dilute aqueous ammonium hydroxide only. From these data, it can be seen that SC-1 alone is inadequate for HMDS removal, and that dilution of SC-1 reduced the HMDS removal efficacy. However, when the diluted SC-1 is used in conjunction with a complete suite of pre-gate cleaning chemistries (as is often the case), dilution of the SC-1 clean did not reduce the overall HMDS removal efficacy, as shown in Figure 6. Finally, since the "Fab Clean" included an aggressive organic stripping clean (piranha), an experiment was performed to evaluate the efficacy of dilute SC-1 for HMDS removal when the piranha clean is omitted from the sequence. Figure 7 shows HMDS removal efficacy in a cleaning sequence that does not include piranha. Various dilutions of SC-1 were evaluated as part of a cleaning sequence that included HF and SC-2. The data of Figure 7 show that all cleans performed equally. Not only did dilution of the SC-1 provide no measureable reduction in HMDS removal (when performed in conjunction with HF and SC-2 cleans), but inclusion of piranha in the cleaning sequence provided no significant benefit for HMDS removal. Overall, these results indicate that SC-1 alone is inadequate for the removal of HMDS, but when a dilute SC-1 is used as part of a pre-gate cleaning sequence that includes HF and SC-2, then dilution of the SC-1 has no deliterious effect on HMDS removal. Omission of the piranha step from a pre-gate clean sequence may also be feasible, as this step provided no additional benefit for HMDS removal when it is included in a full pre-gate cleaning sequence.

A second experiment was performed in which DOP was used as the contaminant challenge to evaluate the efficacy of dilute SC-1 for the removal of light organic material. The surface binding chemistry of DOP differs significantly from that of HMDS in that DOP binds strongly to a hydrophobic silicon surface. The results given in Figure 8 show that for the hydrophilic samples, all the dilutions of SC-1 were highly effective for removal of DOP. For the hydrophobic samples, only the Fab Clean, which included the full suite of pre-gate cleans, resulted in acceptable levels of DOP remaining on the wafer surface. The role of piranha in the "Fab Clean" has not yet been evaluated for DOP removal. The DOP results indicate that light organics with similar binding characteristics to DOP may be easily removed from hydrophilic surfaces, so that aggressive chemistries such as piranha may not be necessary.

C. Environmental Implications

The extent of chemical reduction possible using dilute chemistry SC-1 depends on numerous factors such as the degree of dilution, the bath lifetime (typically at least 8 hours, depending the existence of metallic contamination), and the bath volume. For the purpose of benchmarking several different dilutions against traditional concentration SC-1, a basis of one 20-liter bath poured daily was used. The expected chemical usage for various dilutions is shown in Table 1. Also shown is the percent reduction in chemical usage, compared to a traditional 1:1:5 cleaning chemistry. Clearly, substantial reductions in chemical usage may be obtained through the use of dilute concentration SC-1.

A directly related benefit to dilute chemistry cleaning is the resulting reduction in rinse water required following the clean. Table 2 shows typical rinse times following various cleaning chemistry concentrations. All rinses were performed in cascade overflow mode (no quick dump) until a resistivity greater than 15 MΩ-cm was obtained. As Table 2 shows, a substantial reduction in rinse time, and thus rinse water volume, can be achieved through dilute chemistry cleaning. For example, using a 1:10:100 SC-1 instead of the traditional 1:1:5 resulted in a 41% reduction in rinse water usage.

CONCLUSIONS

Chemistries used in a cleaning sequence are often selected based on historical precedents. Therefore, careful examination of the chemistries and cleaning sequences may be appropriate. For example, by better understanding the performance limits of SC-1 chemistries with respect to particulate and organic contamination removal, significant reductions in chemical usage can be realized.. Substantially diluted SC-1 chemistries can still be highly effective for particle removal, provided sufficient megasonic energy is applied. Zeta potential interactions, rather than silicon etching, appear to be the dominant factors for particle removal; cleaning chemistries which are concentrated enough to provide substantial silicon etch rates need not be used for SC-1 particle removal. The study of light organic contamination removal using diluted SC-1 showed that if the SC-1 is used as a stand-alone process, then a reduction in organic cleaning efficacy may be expected. However, if the SC-1 is used in conjuction with other typical pre-gate oxidation cleaning steps, then the overall cleaning sequence is quite robust, and dilution of the SC-1 has no deliterious effect on organic removal. In addition, for the removal of light organics, omission of the piranha step from pre-gate cleaning sequences may be considered as an alternative process sequence. The omission of this process step should yield substantial chemical and water savings. These results demonstrate that using optimized cleaning sequences can provide effective contamination removal while often resulting in reduced chemical and water usage.

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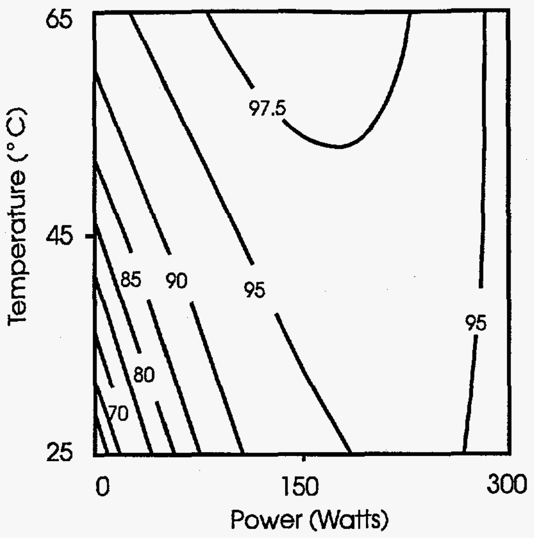

Figure 1. Si_3N_4 particle removal efficiency (≥ 0.11 µm) with $NH_4OH:H_2O_2 = 1.0$

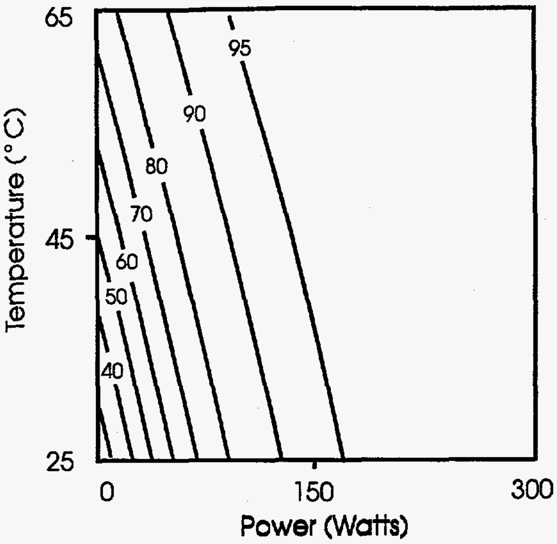

Figure 2. Si_3N_4 particle removal efficiency (≥ 0.11 µm) with $NH_4OH:H_2O_2 = 0.01$

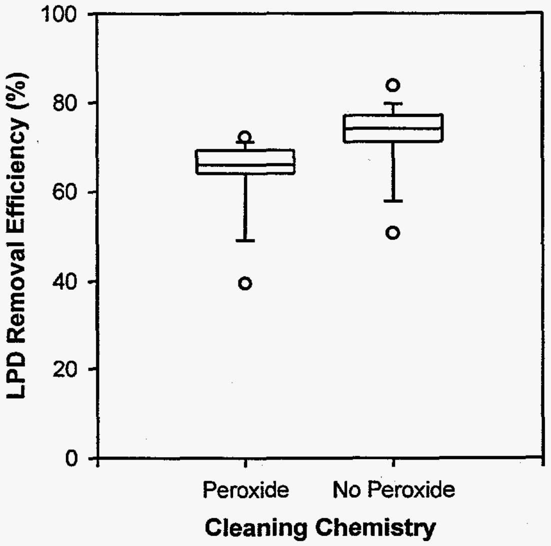

Figure 3. Silicon nitride particle (<0.15 µm) removal in dilute solution NH_4OH chemistries at 45°C, with and without H_2O_2 (1:80:2600 and 1:0:2700, respectively).

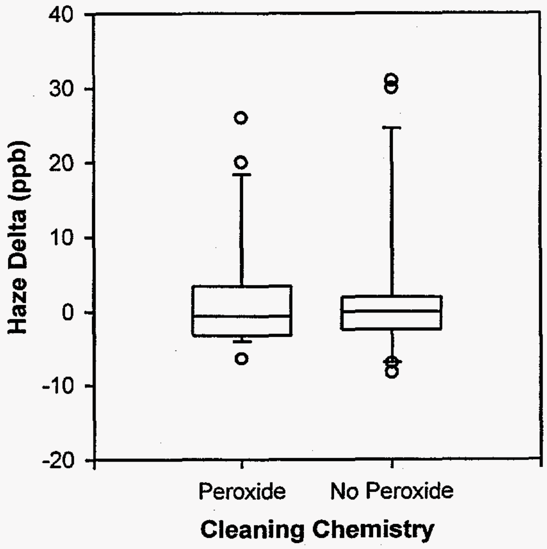

Figure 4. Surfscan 6200 haze measurements following dilute solution NH_4OH chemistries at 45°C, with and without H_2O_2 (1:80:2600 and 1:0:2700, respectively).

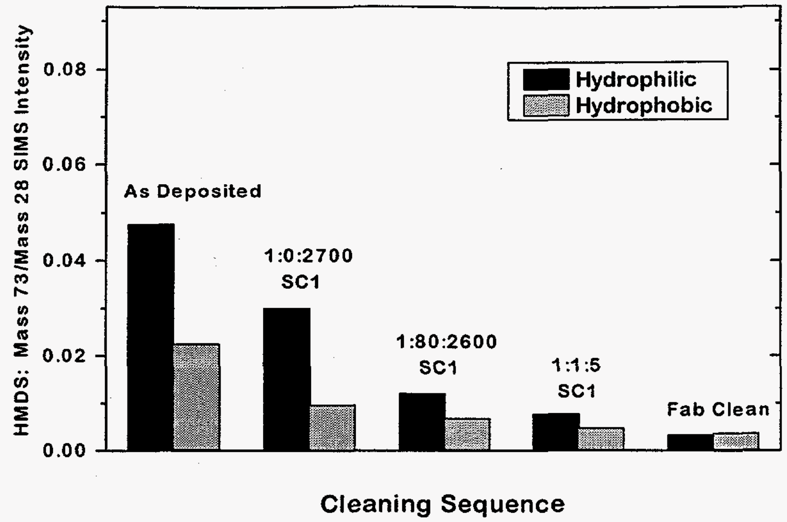

Figure 5. HMDS removal vs. cleaning sequence. As deposited received no clean; Fab Clean received HF, piranha, SC-1, SC-2. All other groups received SC-1 only.

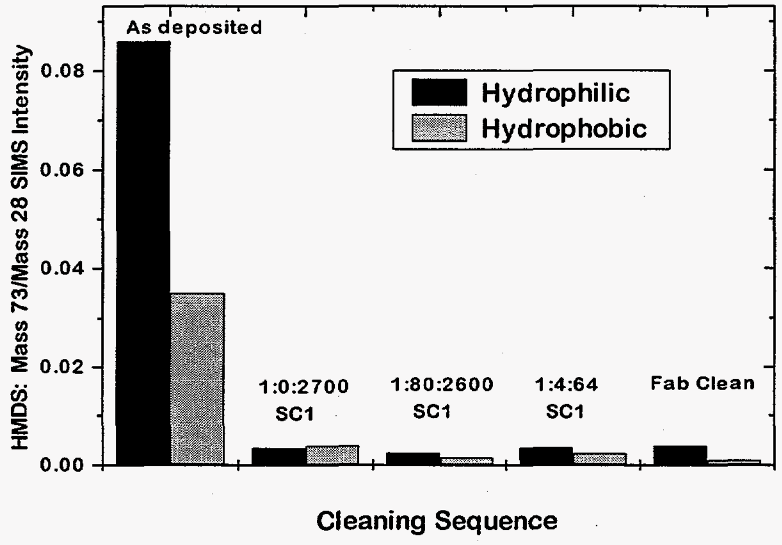

Figure 6. HMDS removal vs. Cleaning Sequence. As deposited received no clean. All other groups received HF, piranha, SC-1, and SC-2 cleans. The SC-1 concentration was varied (diluted).

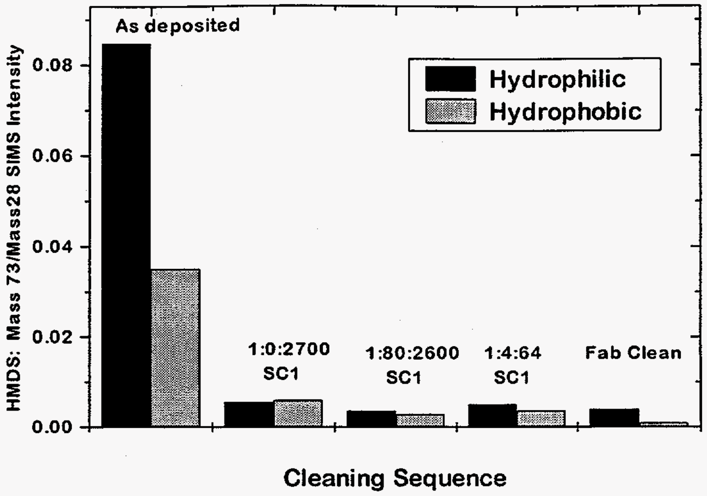

Figure 7. HMDS removal vs. cleaning sequence. As deposited received no clean; Fab Clean received HF, piranha, SC-1, SC-2. All other groups received HF, SC-1, and SC-2 (no piranha).

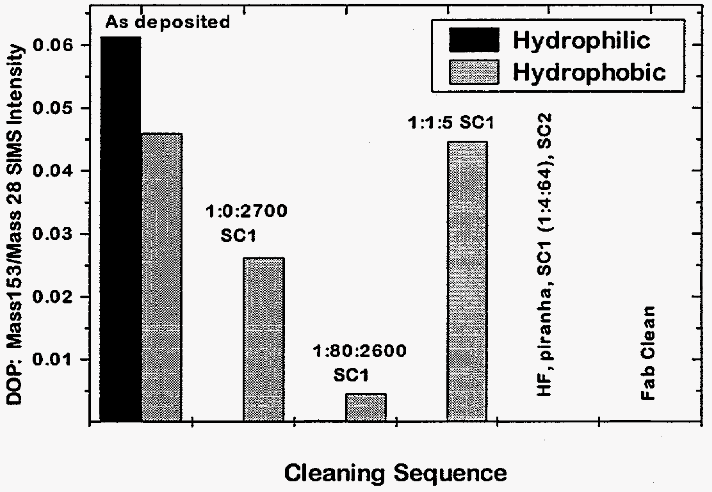

Figure 8. DOP removal vs. cleaning sequence. As deposited received no clean; Fab Clean received HF, piranha, SC-1, SC-2. All other groups received SC-1 only.

Chemical Ratio	NH_4OH Required (liters/year)	H_2O_2 Required (liters/year)	Total chemical reduction relative to tradition 1:1:5 chemistry (%)
1:1:5	1017	1017	--
1:10:100	64	640	65.4%
1:80:2600	3	240	88.1%
1:0:2700	3	0	99.9%

Table 1. Chemical usage of various concentration SC-1 cleaning baths (basis: 20 liter bath poured once per day)

Chemical Ratio	Rinse Time (minutes)	Total water reduction relative to tradition 1:1:5 chemistry (%)
1:1:5	7.0	--
1:10:100	4.1	41%
1:80:2600	<2.0	>71%
1:0:2700	<2.0	>71%

Table 2. Time required to reach rinse effluent resistivity ≥ 15 MΩ-cm.