

# Ultra Low Concentration Clean: A New Approach to Feol Critical Wafer Surface Cleaning

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As the semiconductor industry moves to processes for line widths of 65nm and beyond, there is a need for a new cleaning technology which addresses issues of the nano world, especially the concern of silicon / silicon oxide loss on the devices during each of the cleaning step. Reducing concentrations of ammonia down to a single digit ppm and then to a much lower concentration, makes use of a new dimension of physics: Quantum Electro Dynamics and the formation of "clusters". It is observed for the first time in a semiconductor manufacturing environment that the particles detached from wafer surfaces by megasonic energy, are removed effectively by the zeta potential produced by the "water clusters" enabling us to compare the performance of the clustered clean to the standard RCA clean of the fab.

## Introduction

Clusters of water form on and around solute ions and/or molecules in very dilute solutions and their physical properties has been described by Shui-Yin Lo [1,2] in 1996. Also, Suraj Puri et al. [3] showed, that extremely dilute ammonia solution, can attract particles at a molecular level, using an ammonia solution at 10ppm or higher concentration level. Once the megasonic energy has detached the particles from the surface, the clustered water holds the particles in the fluid as it is creating a zeta potential between the wafer surface and the water borne clusters. This phenomenon prevents the re-deposition of particles back, on to the wafer surface. The particles held in the liquid phase by the clusters, can then be easily transported off the processing chamber by an overflow rinse.

Quantum Electro dynamics teaches us that under certain specific conditions, the structure of water can be changed. The random motion of water molecules - under specific conditions determined by the authors – form water "clusters", that move in a pattern with well defined relative phases as compared to random water. This is known as "coherent" water, or "clusters" of water that have different relative phases as compared to ordinary water. These "clusters," which range from very small (3 molecules of water to 280 molecules of water) attract particles of all sizes especially those particles that are similar to the size of the clusters which are subsequently removed in the rinse and dry processes.

The formation of clusters having been measured and the solution is now defined as “Ionized Molecular Activated Coherent Solution” or for short “iMACS™”.

As silicon processing keeps going down - from 90 nm to 45 nm device sizes - and continues to point towards 32 nm devices and less, it is imperative to move to an alternate mechanism of removing these very small particles without damaging device structures.

The scope of this work was to compare the Particle Removal Efficiency (PRE) of this new cleaning method with a standard RCA clean in a large silicon manufacturing fabrication area.

### **Experimental Procedure**

Experiments were conducted to compare a manufacturing process which has been running for over thirty years in the semiconductor industry, with the newly developed iMACS process.

The cleaning tests were performed in the SC1 bath of a 200mm hybrid RCA cleaning wet bench supplied by Steag [4]. This re-circulating bath is running a standard SC-1 process @65°C and is equipped with a Metronics Megasonics system and an array of transducers attached to the bottom of the bath .

For cleaning efficiency tests 200mm wafers were intentionally contaminated with approx. 4000 silicon nitride particles deposited homogeneously on hydrophilic wafer surface. Particle numbers were determined by a light Scattering S6200 KLA Tencor Equipment @ 0,2µm. Another set of tests were run using particles of silicon dioxide at 78 nm diameter using 200mm wafers which were intentionally contaminated. These particles at 78 nm, were analysed by using the haze measurement and light point defect counts, on the KLA Tencor SP1 tool.

For creating the clustered water the CCS-1000 unit was installed in the clean room next to the RCA system. This system creates iMACS by using a mixture of DI water, less than 5 ppm of ammonia gas and megasonic energy. The concentration of ammonia as measured by CCS-1000 was measured and compared to an in-house chemical analysis. Wafers were processed in the SC1 bath of a 200mm hybrid RCA cleaning wet bench and subsequently processed through a rinse tank and Yield UP STG™ rinse/dry tank, that uses a cascade overflow of DI water followed by a drain step using an isopropyl alcohol-induced surface tension gradient. A hot nitrogen gas drying step completes the drying cycle.

## Results and Discussion

As there was production equipment being used for 24x7, device manufacturing line, the first main focus was to analyze the impact of the newly installed hardware on the production environment. Figure 1 shows that there is no significant rise in defect density when using the new ultra dilute solution (iMACS), compared to the standard SC-1 chemistry mixing unit of the main production Steag system.

### Process Performance Demonstration Results

The PRE for silicon nitride particles for 200 nm size, is shown in Figure 2. For reference, test was performed using Std. SC1 chemistry. The cleaning efficiency of megasonic energy was evaluated by running tests with and without the megasonic energy. Another set of experiments were done by using only DI water with megasonic energy without any SC-1 or iMACS.

The PRE of the clustered clean is comparable to the Std. RCA Clean @65°C. For particles >200nm a PRE of >99% was reached for both iMACS & Std. RCA Clean@65°C, when the shadowing effect of the cassette was removed by moving the wafers through a ninety degree rotation, as shown in Figure 2.

PRE results for 78nm particles are given in Figure 3..The Haze maps given in Figure 4 show the distribution of the cleaning efficiency on the wafer. This distribution is driven by the propagation of the megasonic energy field within the limitations of “Steag” bath, and the cassettes holding the production wafers.

Experimental test results also includes tests with Standard. RCA clean @ 65°C. As for the silicon nitride particles the PRE for the clustered clean is similar to the PRE for a Std RCA clean @35°C.and the PRE of RCA@65°C.

The results from the haze map show that due to the excessively large etch rates of standard RCA clean we get a very uniform cleaning efficiency all the way to the edge of the wafers, even in the areas where there is no effect of the megasonic energy due to the shadowing effect. As we reduce the etch rate effects and go to Standard RCA @35°C,(this RCA solution at 35°C has one tenth the etch rate of Silicon dioxide as compared with the standard solution of RCA at 65°C) we see a distinct reduction in the PRE or cleaning efficiency as compared with that of RCA solution at 65°C. Figure 4 dramatically explains the reason of reduced PRE. Owing to the reduced etch rates at 35°C, and “zero” etch rates for iMACS, the shadowing effect of the Steag cassettes overwhelms the cleaning capabilities of the iMACS. and the standard RCA at 35°C.

Figure 5 gives the removal of deposited types of Silicon Oxide by Std. RCA@35°C, clustered water(iMACS) and deionized water at a process time of 30min. Std. RCA@65°C is known to have 10 times the etch rate of Std. RCA@35°C and therefore cannot be placed within the Figure 5 as it would not fit within the existing scale.. The clustered water etch rates on the other hand, for standard processing time of 3 to 10 minutes, shows no silicon oxide loss.

## Extra Field Data For Comparison Of Ammoniated Solutions And Clustered Solutions:

After completing the production testing at Infineon, other experiments were carried out in the field to compare particle removal efficiency for just Ammoniated water, without forming “clusters”, and using PCT Megasonic system and then comparing the PRE's with a standard batch processing with iMACS.

With the above method Ammoniated solutions with D.I. water and without any clusters, were formulated at ultra low concentrations of Ammonia and then Particle Removal Efficiency were determined using standard batch re-circulating cleaning bath.

Fig 6 clearly shows that with Ammoniated solutions alone, for particles > 200 nm, does not effectively clean the Nitride deposited contamination. From >99% PRE as reported by Infineon in this paper, for clustered cleaning for particles > 200 nm, just ammoniated solutions without “clusters”, cleans an average PRE of ~50% for 0.10 ppm of ammonia concentrations.

In order to study the formation of clusters further, extensive tests have been done to measure the presence of “clusters” by inventing a technique based upon the differential absorbance signal of the activated (clustered) solution, from the absorbance signal of non activated(no clusters) solution, with the same ionic components in the two solutions. This differentiation leads to a clear residual absorption signal which is used as a measure of the quantity of clusters in the water.

## **Conclusions**

The clean by clustered water has been shown to have the same PRE as Std. RCA procedures @ 35°C and @ 65°C. Yet there is a significant difference in the removal rate of Silicon oxide.

As the integration race goes on towards low or no substrate loss, etch rates in cleaning will be one of the key factors to a successful wafer cleaning strategy. This makes the clustered clean by Nano Green Technology Inc. a very interesting new alternative for addressing the technology needs of today's cutting edge production and the requirements of the years to come.

## **References**

1. Lo SY., “Anomalous State of Ice” Modern Physics Letters B 10, 909 – 919, (1996)
2. Lo SY., “Physical Properties of Water with IE Structures” Modern Physics Letters B.10, 921 - 930, (1996)
3. Suraj Puri et al., “An Ultra Dilute Ammonia Process for Particle Removal” The Electrochemical Society Proceedings Volume 99-36, 180
4. Handbook STEAG AWP tool,

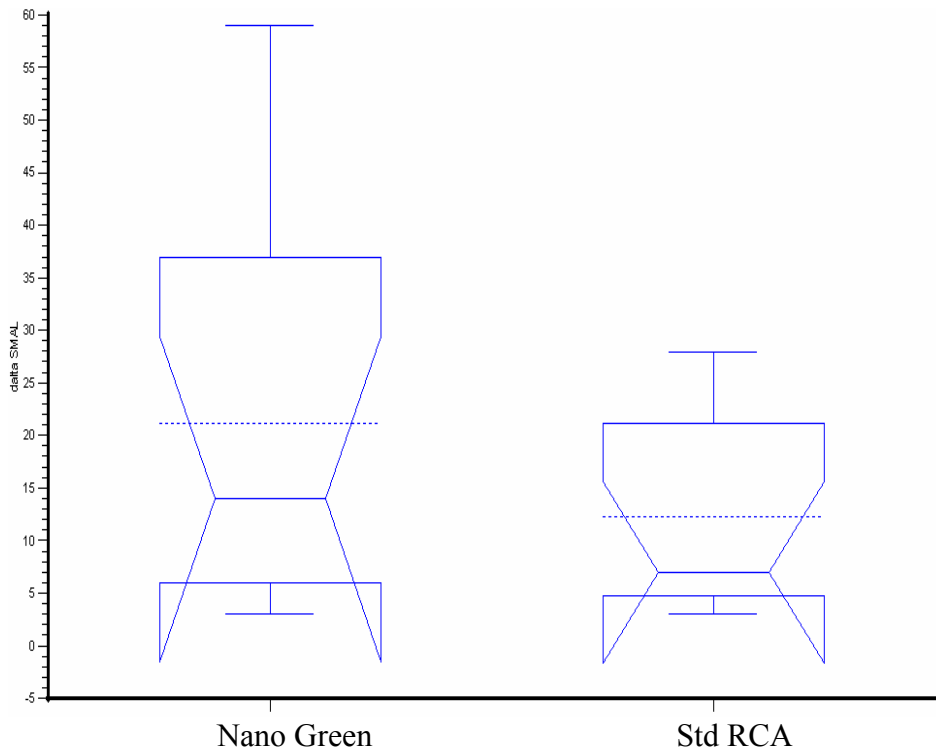


Figure 1: Comparison of defect density of clustered water to standard RCA clean

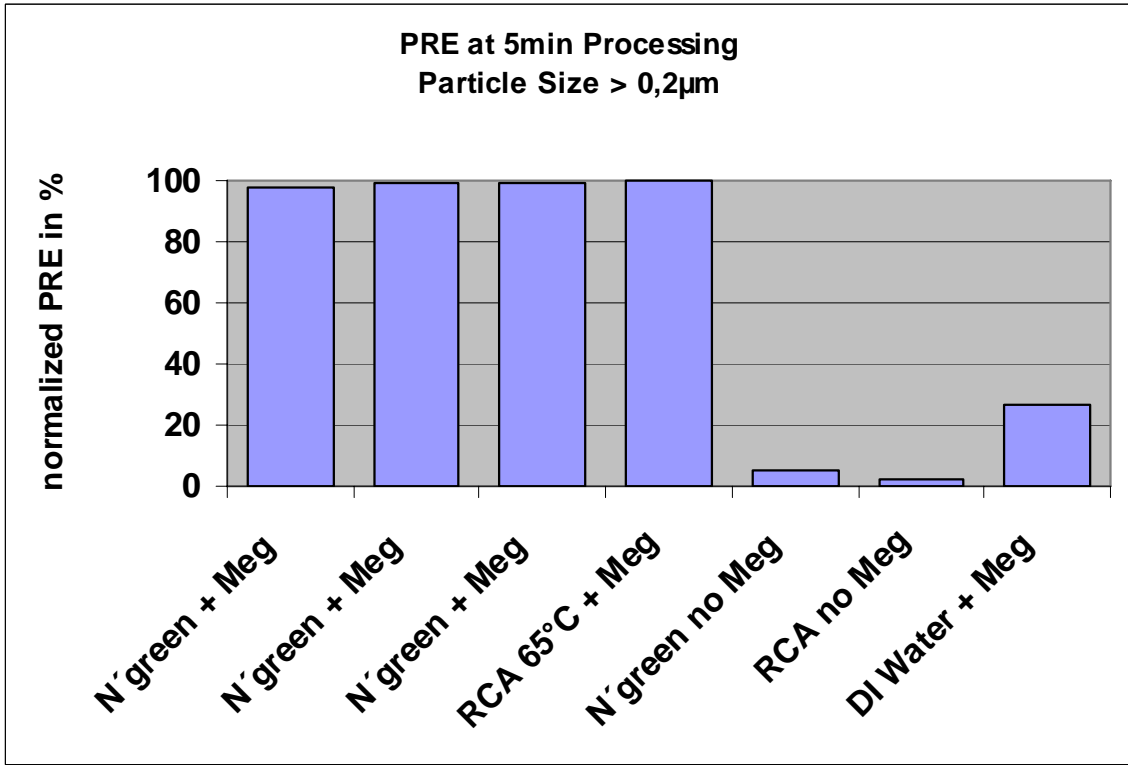


Figure 2: PRE for clustered water and standard RCA clean @ 65°C

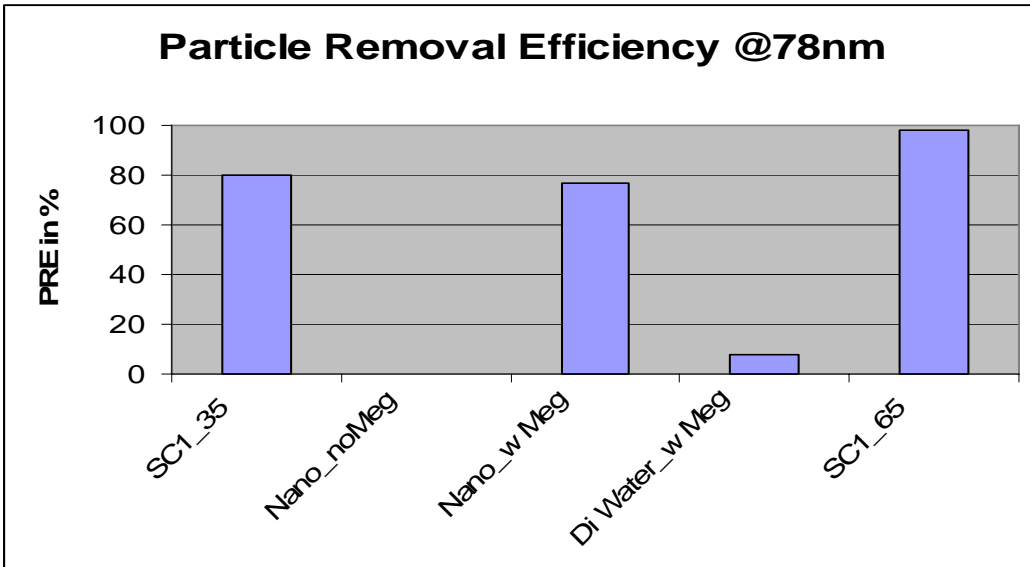
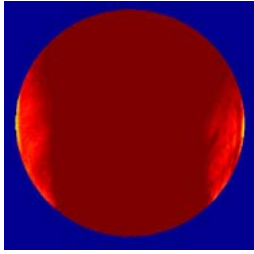
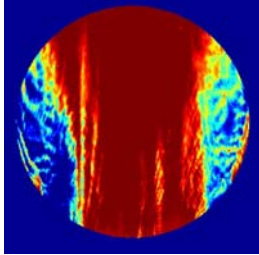


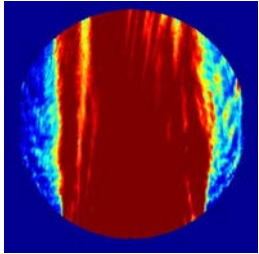
Figure 3: PRE for clustered water vs standard SC-1 @ 65°C and @ 35°C



SC-1 @ 65°C



Cluster clean



SC-1 @ 35°C

Figure 4: Haze maps for 78 nm oxide particles, with shadowing problems

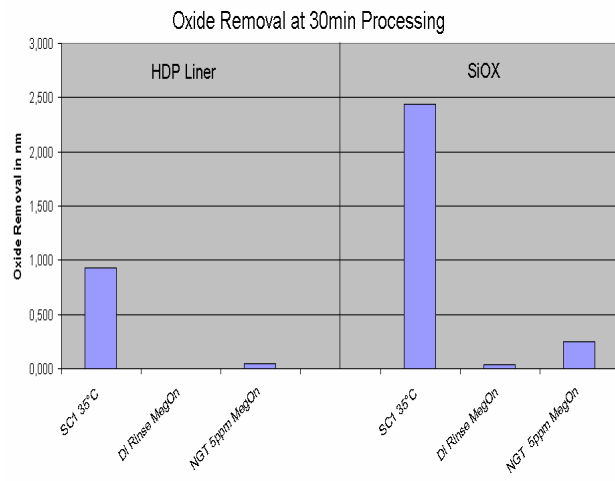


Figure 5: Oxide Etch Removal For SC1 @35°C and Clustered Water

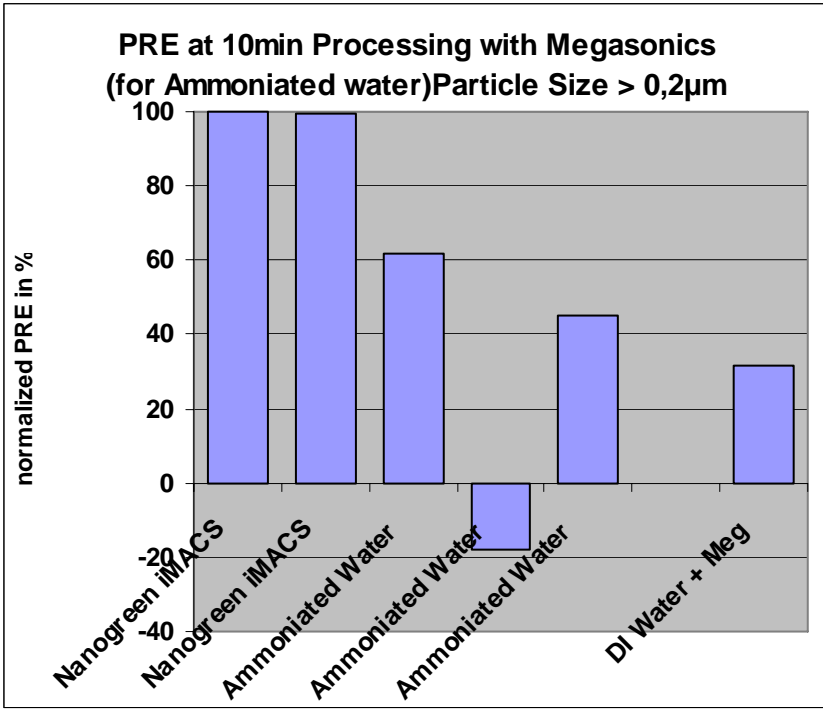


Figure 6: Comparison of Ammoniated water to iMACS