

# Mask Cleaning Strategies—Particle Elimination with Minimal Surface Damage

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## ABSTRACT

Cleaning becomes increasingly important and challenging as feature sizes continue to shrink. Many methods and strategies have been explored to reduce particle defects and ion haze that destroy yield on pelliclized reticles. A successful cleaning method must balance reductions of particles and haze while imposing minimal changes to the transmissivity of the chrome stack, to exposed quartz and to the phase shift of molybdenum silicide surfaces. This paper focuses on the inclusion of many previously explored cleaning methods working in concert within a single reticle cleaning tool. We present our findings on elimination of particles with minimum impact on reflectivity and phase angle. We test the collective effects of Ozonated Water (O3W) and final cleaning methods that employ ammonia hydroxide and hydrogen water. These methods are presented within the context of spin cleaning applications.

## INTRODUCTION

Sulfate and ammonia ion residues have been linked by others to contamination growth and lifetime improvements can be gained by reduction of such residuals on the reticle through enhanced cleaning techniques. Eliminating these residues during mask cleaning is an important step forward. The replacement of sulfuric acid in the final cleaning process is an obvious means for ion reduction. Eliminating ammonia and hot water will benefit molybdenum silicide (MoSi) and quartz durability. Therefore, the greatest step forward may be to avoid high concentrations alkalines and acids and apply low concentration reagents at room temperature (20-21C).

Tables 1 and 2 below show previously published results for changes in Phase Shift and Transmission due to different methods of cleaning MoSi Embedded Attenuated Phase Shift Masks (EAPSM).

Item	Samsung <sup>1</sup>	DPI/TX <sup>2</sup>	DPI/TX <sup>2</sup>	DPI/Akr <sup>3</sup>	DPI/Akr <sup>3</sup>
Phase Shift deg/clean	0.39	0.45	0.17	0.07	0.7
Trans Shift %/clean	0.036	0.22	0.025	-	0.05
Cleaning Conditions	Diluted NH4OH	Wet	UV/Wet	DIO3/SC1 22C Rinse	DIO3/SC1 70C Rinse

Table 1: Previously reported Phase Angle and Transmissivity shifts that occur with different cleaning techniques.

Item	Top/CHN <sup>4</sup>	DPI/Kor <sup>5</sup>	Intel <sup>6</sup>	Intel <sup>6</sup>	Top/Mitsu <sup>7</sup>
Phase Shift deg/clean	0.16	0.62	0.65	0.2	0.1
Trans Shift %/clean	0.02	0.04	-	-	0.02
Cleaning Conditions		35C DI	SPM/UV/ NH4OH	SPM/UV/ UD SC1	Bath not Spin

Table 2: Previously reported Phase Angle and Transmissivity shifts that occur with different cleaning techniques.

The new data presented here is from a Sigmmelec MRC3000 Mask Cleaner. The MRC3000 uses spin processes versus bath processes. Each method has its valuable features. Spin cleaning systems have the advantage of providing a means of delivering a continuous flow of clean reagents to the plate. The spin method also provides centripetal shear forces to particles adhered to the plate which can assist in efficient particle removals and reduced ion residues. Our work here looks exclusively at room temperature spin cleaning processes. We apply reagent combinations dynamically. We use streaming flows and megasonic flows versus spray.

### Methods of Particle Removal

Three process types were applied for particle removal. Each has its own associated wear characteristics for chrome and MoSi surfaces.

#### *Megasonic Energy with Plate Spin*

Megasonic cleaning is now common. Delivering various reagents through the megasonic is relatively new and will improve its particle removal characteristics. Applying dissolved H<sub>2</sub> gas in deionized water (DI) through the megasonic weakens the vanderWaal forces adhering a particle to the plate and of course leaves no residue. Because our cleaning process involves spin, we can apply centripetal shear forces which are linearly proportional to the rotation rate. Simultaneously, the acoustic vibrations from the megasonic can help to push the particle vertically up from the plate and further weaken short range forces binding the particle. Sustaining this megasonic acoustic vibration in the presence of the shear force imposes a direction off the plate for particles that would otherwise experience an aimless acoustic migration.

#### *The Excimer UV Exposure with 172nm*

The use of 193nm light has been observed to supply activation energies for ammonium sulfate crystal growth. Excimer emissions at 172nm have been shown to supply activation energy more than sufficient for ammonium sulfate crystal formation. This wavelength is also known to destroy the cross linking of organic bonds that can hinder plate wet ability.

#### *Ozonated Water*

Ozonated water (O3W) plays a role in industrial disinfection and neutralization of organic wastes. We use O3W in mask cleaning for its ability to oxidize organic residues that can prevent intimate wetting of the plate. Gim Chen *et al.*<sup>3</sup> report effective use 70C O3W in an immersion process for resist stripping. Koji Tange *et al.*<sup>7</sup> report chrome contact angles of O3W that are 4 fold more relaxed at 50C than at room temperature. Wetting characteristics are improved at higher temperatures.

## RESULTS

### Particle Removal

#### *Megasonic*

The megasonic, in conjunction with spin, was the most powerful “surface-safe” cleaning agent we could apply for silicon nitride particle removals. The MRC3000 can accommodate a number of different reagents and reagent combinations through the megasonic head. Several different reagent combinations were investigated. The premier performer was H<sub>2</sub> water with ultra dilute ammonium. This combination seems to supply a good balance of reducing and oxidizing dissolved gas components at the proper concentrations<sup>8</sup>. Figure 1 shows a 99.2% removal efficiency for silicon nitride (SiN) particles when the megasonic was used with ultra dilute H<sub>2</sub> and ammonium hydroxide.

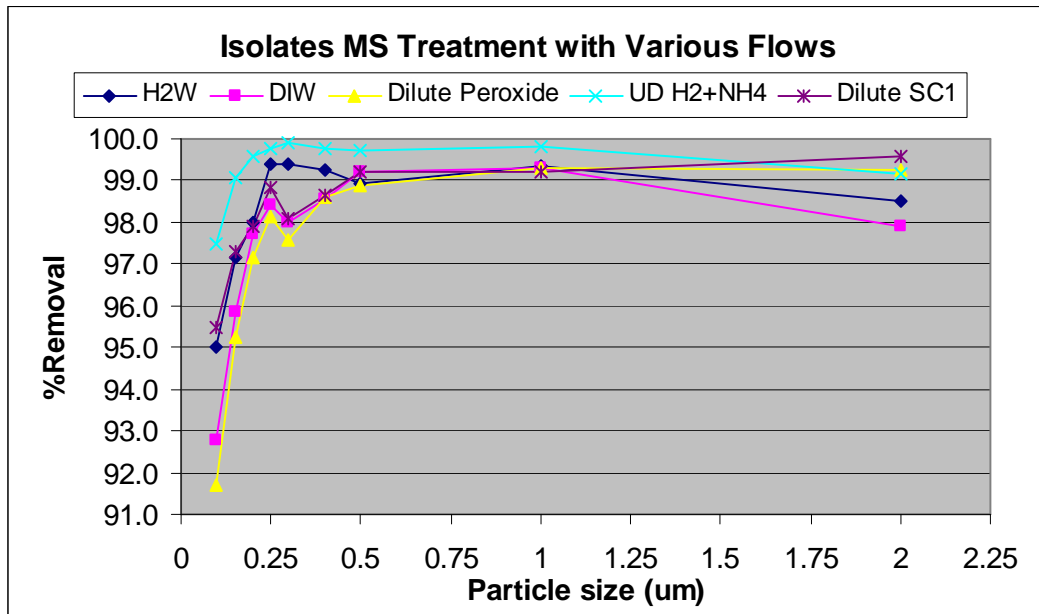


Figure 1: Shows a 99.2% removal efficiency for silicon nitride (SiN) particles when the megasonic was used with ultra dilute H<sub>2</sub> and ammonium hydroxide.

#### *The UV Chamber*

The initial use of the UV chamber in our process is to improve wettability. Some particle types can be volatilized by 172nm UV radiation during this step as well. The details of this process are not well understood. Figure 2 shows an SEM image of a carbon particle / residue with its Energy Dispersive X-ray (EDX) spectra representative of the particles which can be volatilized within the UV environment. Figure 3 shows the removal efficiency vs. time of a plate densely packed with such particles. Figure 4 shows the removal responses of these particles to different gas mixtures within the UV chamber.

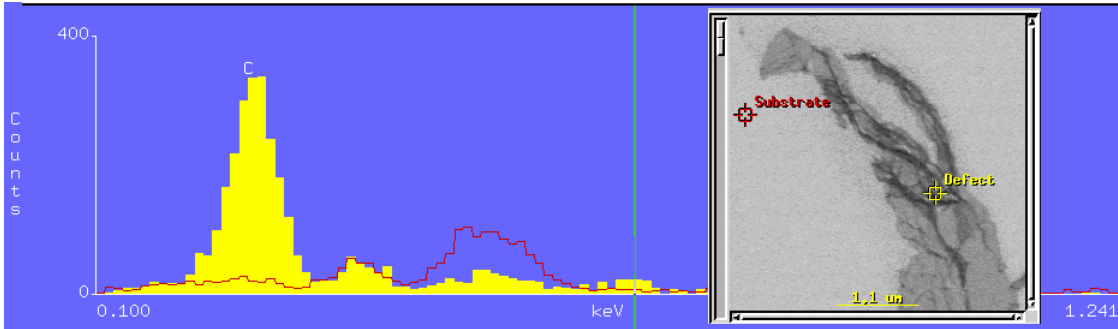


Figure 2: Shows an Energy Dispersive X-ray (EDX) spectra of carbon particles which can be volatilized within the UV environment.

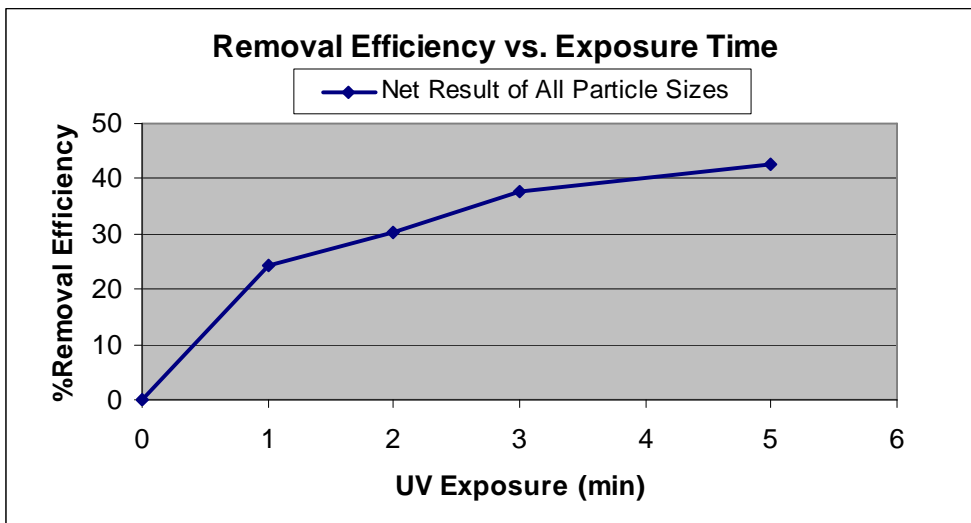


Figure 3: Shows the removal efficiency vs. time of a plate densely packed with such particles.

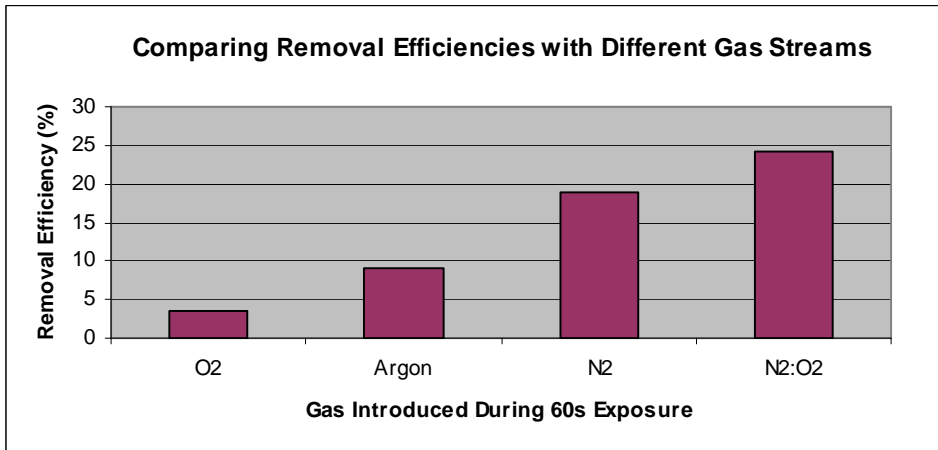


Figure 4: Shows the removal responses of these particles to different gas mixture within the UV chamber.

### Ozone Water

Ozone water can be helpful in oxidizing organic films. With the MRC300 it can be applied at varying concentrations. Removal efficiencies were tested within the context of a full cleaning routine. This consisted of UV, O3W and megasonic treatments. Figure 5 shows removal rates for silicon nitride particles at 3 different O3 concentrations for this cleaning sequence. Particle removal rates were observed to decrease at the higher concentration C. An optimum concentration was defined and used for all further particle testing.

Using the optimum concentration, the O3W process was isolated for its contribution to the overall particle removal efficiency. By itself, it removed less than 5% of silicon nitride particles. Two different spin speeds were tried to determine if the particles adhesions could be overpowered by increasing the spin shear force on them by six fold<sup>9</sup>. Particle removals were not greatly improved. The results are displayed in Figure 6.

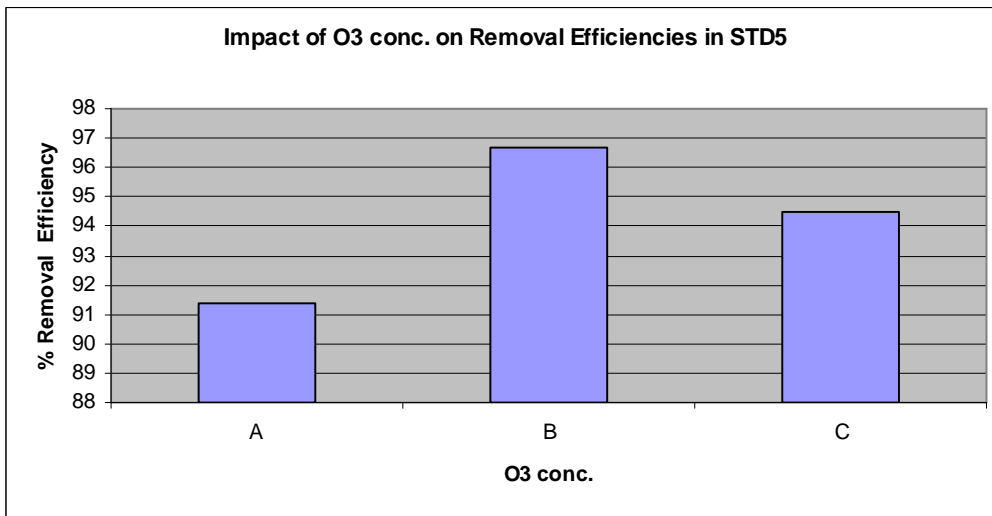


Figure 5: Shows removal rates for silicon nitride particles concentrations A, B, and C of ozone water within the context of a complete cleaning recipe.

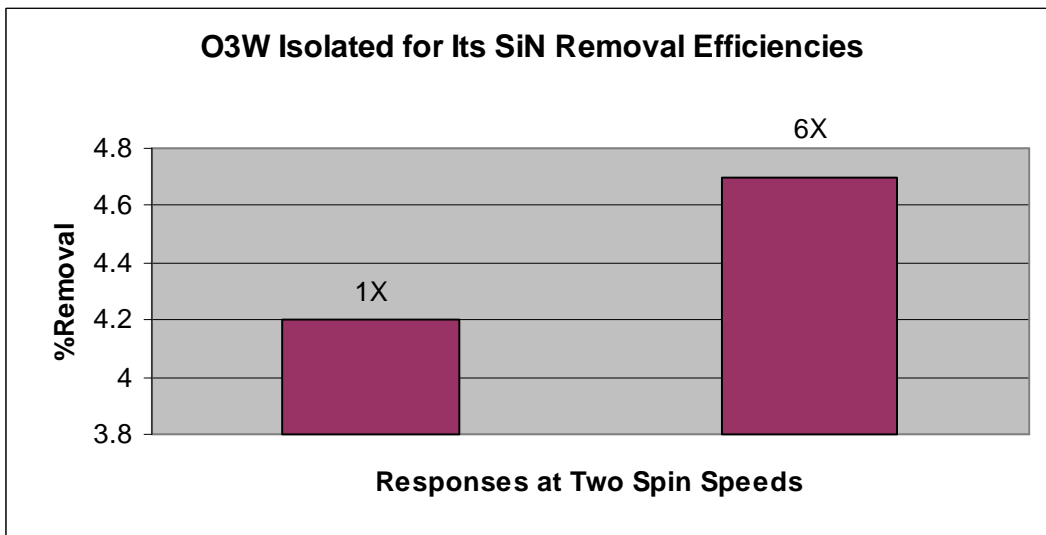


Figure 6: Ozone water alone removed less than 5% of SiN particles.

**ARC Loss**

The surface of a chrome mask is composed of a sputtered film. Metallic chrome is topped with an Antireflective Coating (ARC) that transitions from chrome oxide (CrOx) at the bottom to chrome oxynitride (CrOxNy) at the surface. This film varies continuously from top to bottom. Consequently, rates of removal for the ARC surface can vary with material susceptibility and content at the cleaning surface. Data was collected for each process from masks with the same chrome stack height.

Figure 7 shows the ARC wear from each of the three cleaning processes. ARC changes during the UV process were measured by both N&K and nano-profilometry. Nano-profilometry could corroborate only two-thirds of changes reported by N&K. Ozone water was by far the largest offender for chrome loss.

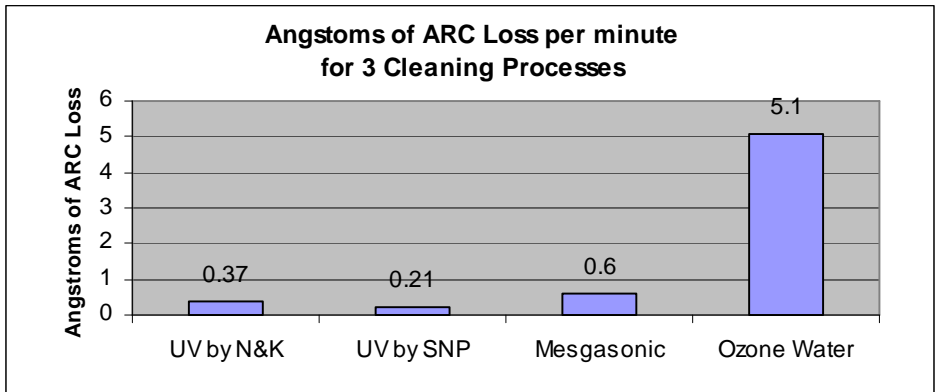


Figure 7: Shows the ARC wear from each of the three cleaning processes.

**Reflectivity Changes in the Chrome Stack**

Figure 8 displays the individual contributions to reflectance changes at 193nm and 248nm for 1) UV treatment (172nm), 2) megasonic treatment time and 3) the O<sub>3</sub> water contact time used in our recipe. The last column set describes the collective impact of all three process steps.

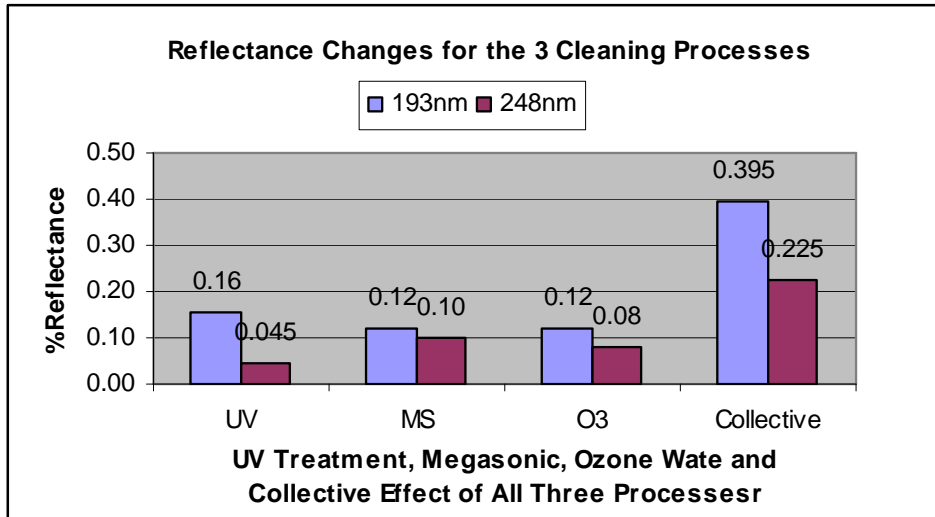


Figure 8: Displays the individual contributions to reflectance changes at 193nm and 248nm

**Transmissivity Changes in the Chrome Stack**

Figure 9 shows the Transmissivity changes in the chrome stack for each of the three cleaning processes. The final column set describes the total amount of Transmittance change that occurs with the contact times and exposure times that occur within the recipe.

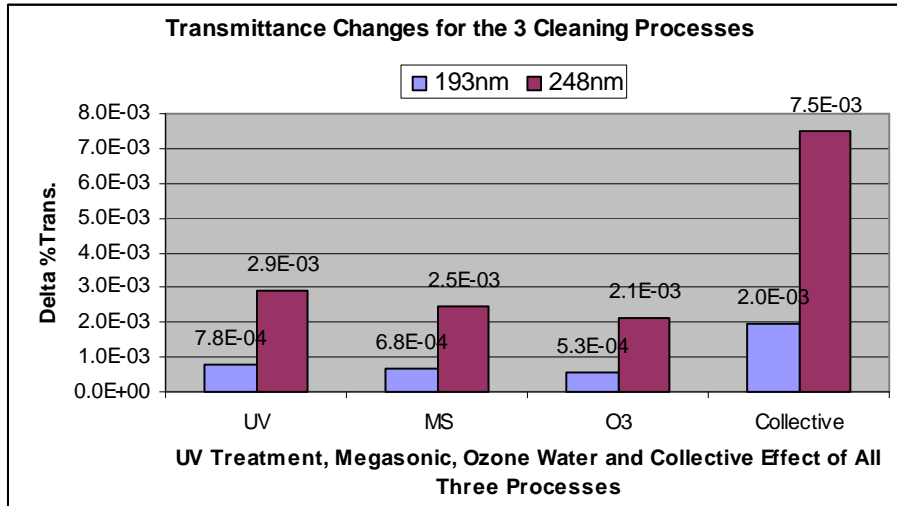


Figure 9: Shows the Transmissivity changes in the chrome stack for each of the three cleaning processes.

**Phase Angle damage to MoSi**

As discussed above, we found our best particle performance with hydrogen water and ultra dilute ammonia (H<sub>2</sub>+UD NH<sub>4</sub>). To retain this level of particle performance and keep our losses of molybdenum oxides low is problematic. Our review of literature informed us that the use of hot water and ammonia would be damaging for the MoSi surface. Figure 10 displays the comparison of MoSi phase angle change that occurred when using H<sub>2</sub> alone in the megasonic stream versus H<sub>2</sub>+UD NH<sub>4</sub>. Figure 11 displays the changes in transmission we recorded for these same two reagents.

Qualitatively, our results were consistent with other researchers. Quantitatively, the low levels of MoSi damage are outstanding when compared to the literature values displayed above in Figures 1 and 2.

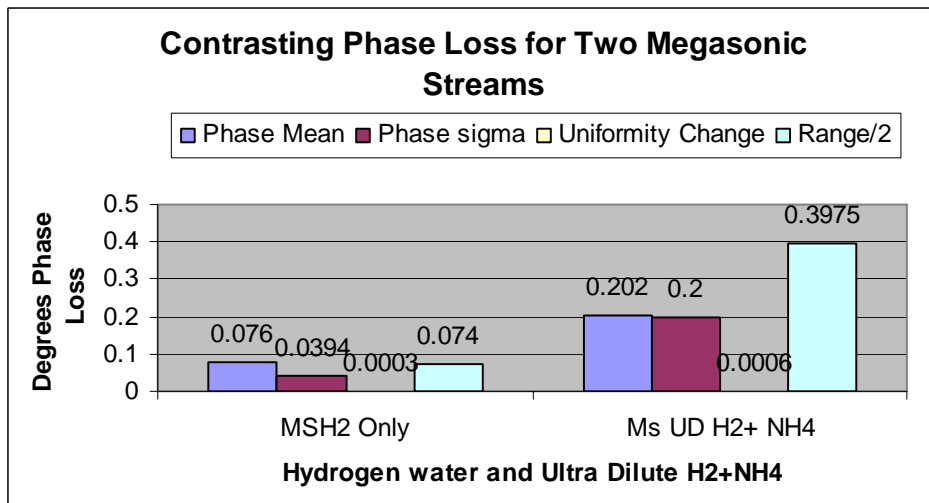


Figure 10: Shows the Phase Angle loss associated with contact times within the recipe.

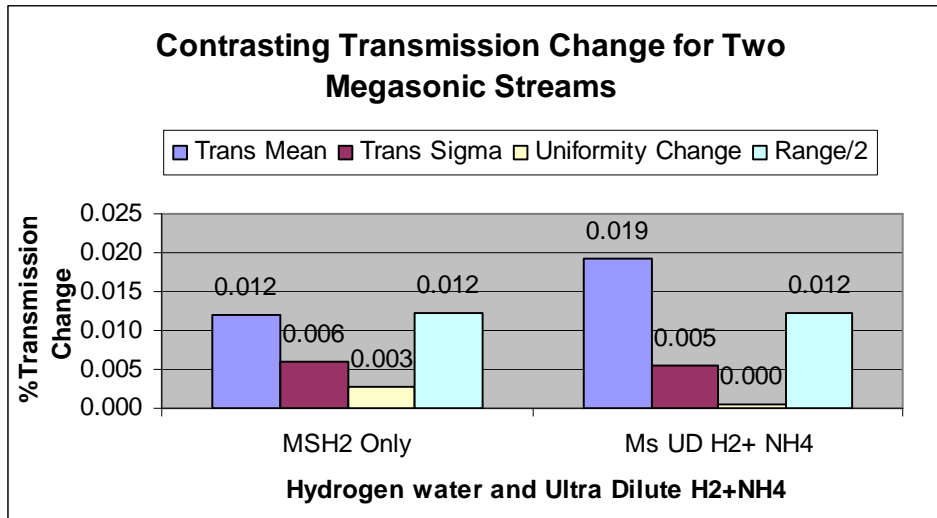


Figure 11: Displays the changes in Transmissivity associated with contact times within the recipe.

Figure 12 displays the phase angle and transmissivity changes that occur with two of the three process types used in our recipe. UV is not included in this comparison because the data was not complete at the time of publication. The UV process is known to build molybdenum oxides. Rather than increasing phase angle and transmissivity changes, its use in concert with low concentration alkalines and room temperature water can build a passivating layer that slows the rate of phase angle and transmissivity change with repeated cleanings<sup>6</sup>. The Collective column of Figure 12 accounts for both process types added together. These values are representative of the wear to an EAPSM with our Recommended Recipe.

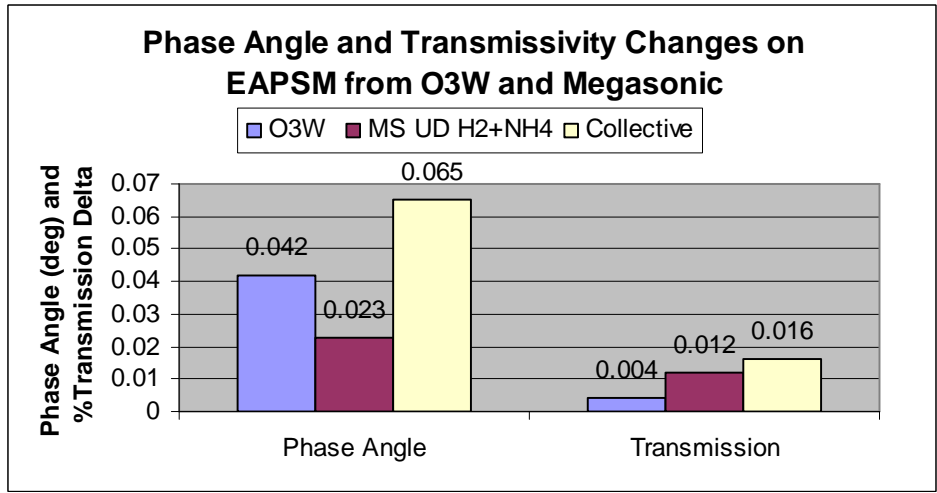


Figure 12: Phase angle and transmissivity changes that occur with two of the three process types used in our recipe. The Collective column accounts for both process types added together. These values are representative of the wear to an EAPSM.

### ***Structural or Feature Damage***

All cleaning involves some wear to the mask. Understanding the types and severity of damage that can occur allows one to create an ideal cleaning routine. We observed structural damage on plates caused by inappropriate cleaning parameters (Figures 13)

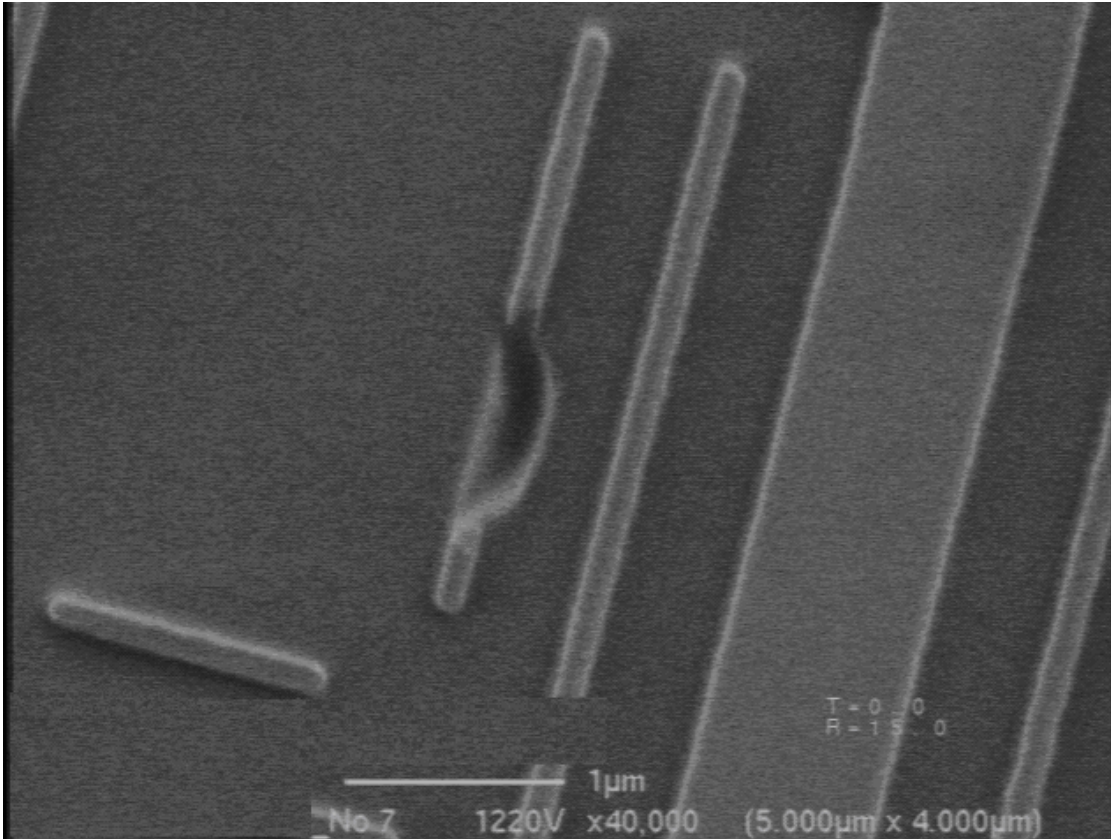


Figure 13: Shows an instance of scatter bar damage. Understanding the types and severity of damage that can occur allows one to create an ideal cleaning routine.

## **CONCLUSION**

We have discussed room temperature cleaning—its impact on chrome and MoSi surfaces. We have found that it is possible to have 99+% cleanings of SiN particles while obtaining world class phase shift and transmissivity figures (Figure 14). With this level of low damage quality cleaning, more cleanings are possible with fewer defects.

<b>Item</b>	<b>DPI/Akr<sup>3</sup></b>	<b>DPI/Akr<sup>3</sup></b>	<b>Top/Mitsu<sup>7</sup></b>	<b>Sigmameltec MRC3000</b>
<b>Phase Shift deg/clean</b>	<i>0.07</i>	<i>0.7</i>	<i>0.1</i>	<i>0.065</i>
<b>Trans Shift %/clean</b>	-	<i>0.05</i>	<i>0.02</i>	<i>0.016</i>
<b>Cleaning Conditions</b>	<b>DIO3/SC1 22C Rinse</b>	<b>DIO3/SC1 70C Rinse</b>	<b>Bath not Spin</b>	<b>Room Temp Spin</b>

Figure 14: We have demonstrated it is possible to have 99+% cleanings of SiN particles while obtaining world class phase shift and transmissivity figures.

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