Mask Cleaning Strategies—Haze Elimination

Steve Osborne[a], Matthias Nanninga[b], Hidekazu Takahashi[a], Eric Woster[a]

[a] Sigmameltec Ltd, 3-37-7 Shimoassao, Asao-ku Kawasaki , 215-0022 Japan,
steve.osborne@sigmameltec.co.jp
[b] Advanced Mask Technologies Center, Raehznitzer Allee 9, 01109 Dresden, Germany.

ABSTRACT

A great deal of work has been done on identifying the sources of reticle haze. Researchers have sited haze contributions from the atmosphere, from pellicle, pellicle adhesive and from sulfate residuals left by mask cleaning. Residual sulfates from otherwise high performance cleaning processes can range from 30 ppb and up. This paper focuses on final clean methods within a single track tool that leave concentrations of ion residues approaching 1 ppb. We compare different spin processes which use ozonated water and ultra dilute ammonia and hydrogen water through a megasonic head. Other sources of haze producing ions may remain but eliminating contributions from the final cleaning process opens a productive path to higher yield with 65 and 45 nm design rules.

INTRODUCTION

Researchers have previously sited haze contributions from the atmosphere, from the pellicle, pellicle adhesive and from sulfate residuals left by mask cleaning[1, 2, 3]. These provide the raw materials of haze. One might define haze as the assembly of crystals from ionic constituents adhered to or embedded in the photomask surface which impairs the full lithographic fidelity of image transfer. There is now an industry wide understanding that haze is a product of photochemical reactions influenced by wavelength, total energy, surrounding atmospheric gases and moisture and the presence of compatible ionic constituents for growing nano-crystals. Therefore the ideal cleaning process is one that avoids or somehow controls substances that provide these raw materials. The processes discussed here do not use sulfuric acid. They also do not use hot water. Hot water, although very good at leaching sulfates, has a wear component for quartz and the molybdenum oxide passivation layer of molybdenum silicide (MoSi). The guiding interests of our search for ways to eliminate haze began with the quest for zero particles, for minimal Phase Angle change and for minimal Transmissivity changes. It has evolved towards a "room temperature" process (20-21°C fluid flows) that is capable of eliminating sulfate and ammonium based haze to lithographically insignificant levels.

We have eliminated the use of sulfates within our cleaning process. Those sources of sulfate ion that are external to our process arise from sulfuric-peroxide resist striping and pre-cleaning activities. Eliminating the ammonium cation from our process is not possible. We report in our sister paper "Mask Cleaning Strategies—Particle Removal with Minimal Surface Damage" that 99+% removals are possible for silicon nitride (SiN) particles. The methods used employ ultra dilute ammonia. Without this oxidant/surfactant in our megasonic cleaning solution this level of particle elimination is not possible. But ammonia has key relevance to sulfate removal.   Our work informs us that ammonia is a byproduct of reactions taking place in the ultra violet (UV) chamber[4].

If our UV chamber is generating ammonia, then we have the opportunity of purposely forming crystals long before pelliclization as a strategy for early removal. Our UV chamber operates with a 172nm excimer laser that would have ample energy to drive this surface photochemical reaction. The resulting nano-crystals might be more easily removed during the final rinse step than their smaller un-agglomerated constituents. This constitutes our removal strategy. Johnstone *et al*[1] observed that "volatile ammonia in the air—even in trace amounts was drawn to sulfates on the surface". Volatility, in this case, can mean that ammonia has the ability to move about on the plate with greater freedom than the sulfate ion. Therefore it would make chemical encounters until it finds its kinetically or

thermodynamically stable home. In this sense ammonia can be used as a "getter" for sulfates *before* sulfate crystals create haze.

You will see a few details in our results. Some specifics can't be revealed for proprietary reasons. The data is discussed in a general sense.

EXPERIMENTAL

The Analytical Method for Testing of Ion Residues

Each photomask is placed in a pre-cleaned polypropylene container with a mask pick and leached three times with ultra pure water (UPW) at 50C for 10 minutes each. The UPW extracts are combined in a pre-cleaned bottle for Ion Chromatographic (IC) analysis. Two pre-cleaned extraction containers are prepared and analyzed as controls in the same way as the sample. After the extraction, the photomasks are blown dry with filtered nitrogen in a Class 100 hood and placed back into the original compact. The analysis area is the entire chrome surface of the mask. The back is not analyzed. The photomask leaching process is performed in a Class 100 cleanroom with special chemical filters to minimize contamination of samples during preparation and leaching. Strict cleanroom protocols are followed at all times.

The instrument used for analysis is a Dionex DX-500 Ion Chromatography System equipped with a GP40 gradient pump (anions) or IP20 isocratic pump (cations) and a CD20 conductivity detector. The sample is pre-concentrated on AG11 and CG12A concentration columns, and then separated on AS11 and CS12A analytical columns using sodium hydroxide gradient elution for anions and isocratic sulfuric acid elution for cations. The IC is calibrated semi-annually with calibration standards made from high purity salts containing target anions and cations. Quality control standards, prepared daily from NIST anion and cation standards, are run to verify the instrument calibration before and during sample analysis.

Transportation of the Masks for Residue Testing

Each mask is packaged in a clear plastic shipping box and double bagged to limit air exchange during shipment. The cleaning and preparation for these boxes is proprietary.

Method detection limit:

Method detection limits are typically 0.05 ppb/150 mL for all anions and cations.

Precision and Accuracy:

The accuracy and precision of the analytical results are ±20-30% near and at the above method detection limit levels. At the quantitation level of 0.5ppb the precision and accuracy improve to better than ±15%.

Data Processing and Calculation

Analytical results are entered into an application program worksheet and the concentrations are calculated using the following formula:

(Surface Concentration) / (ppb/150 mL) = $(C_P - C_B) \times V_f$

Where:
C_p = measured concentration (ppb) in the part extract
C_B = measure concentration (ppb) in the solution blank or control
V_f = volume factor (volume of the extraction solution (mL)/150)

Quality Control

A QC standard is analyzed at the beginning and at the end of the analysis sequence. The accuracy of each element in the QC standard must be within ±10% of the nominal concentration after blank subtraction, otherwise the data are QC recovery corrected or the analysis repeated.

RESULTS

Kinetics Wins over Thermodynamics

Ammonium sulfate crystal formation is exothermic. Heat is a byproduct of this reaction. This compound is unusual in this respect, as crystals formed with metallic cations more commonly take on heat during crystal forming. The presence of the molecular cation makes the difference. Thermodynamically speaking, if heat energy is given off by this reaction, then supplying heat would slow the reaction. However, when we tested ion removals with a cooled plate during UV treatment we instead saw a reduction in our removal efficiency. Figure 1 shows how effectively cooling the plate *did not* work for sulfate removal. The high temperature plate had 78% lower sulfates then the ambient plate. Three possibilities exit: 1) ammonium sulfate formation is not a big contributor to our removal process; 2) the kinetics of ammonia sulfate formation relies heavily on ammonia's presence and volatility; 3) this heat provides greater mobility of subsurface sulfates to migrate to the surface where they can react and later be removed. Greater mobility for these species to find one another is key. Interestingly, Figure 1 shows the ammonia concentration found on the high temperature plate was very high in relation to the ambient plate but the incoming concentrations of ammonia and sulfate for both these plates would have been nearly identical.
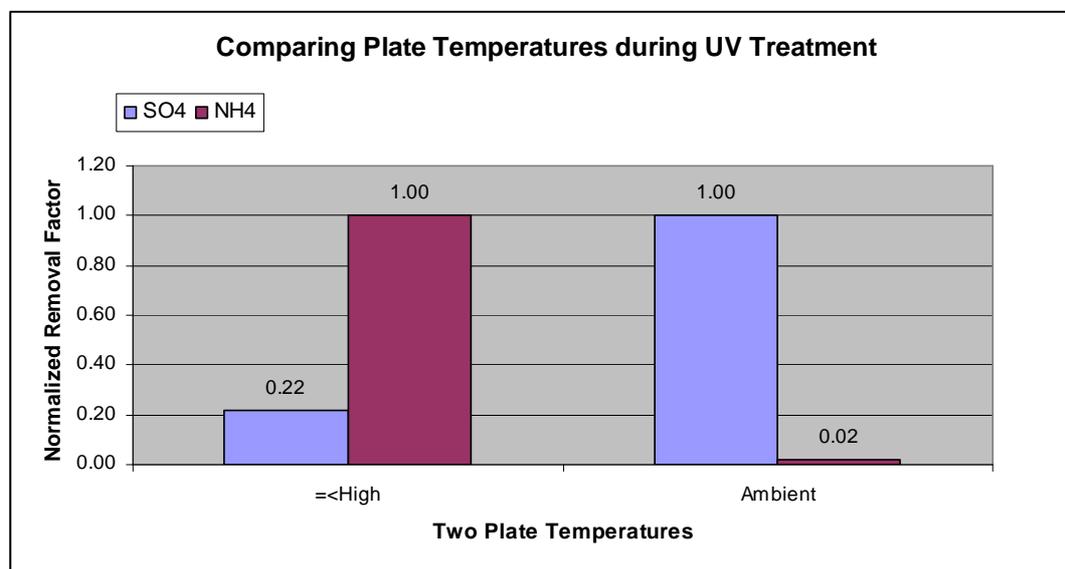

Figure 1: Shows a 78% improved removal of sulfate over the ambient plate, whereas ammonia was 98% higher on the heated plate.

The Influence of UV Atmosphere on Ion Removal

Sulfate
In this test series Gas A is clearly superior to Gas B for removal of sulfate. However, the difference between Gas A and Gas Mix is small and is lost in experiment noise.

Ammonia
The same experimental series shows us what appears to be a clear trend for increased ammonia with the higher concentrations of ammonia's constituent elements in the Gas-Mix. The implication is that when the conditions for manufacturing ammonia have increased, so has the concentration of ammonia. Nitrogen and oxygen alone will form reactive nitrogen species but will not form ammonia. Gas-Mix contains no hydrogen, but small amounts of hydrogen could come from surface moisture and "dangling" free hydronium commonly sited as the cause for plate non-wet ability.
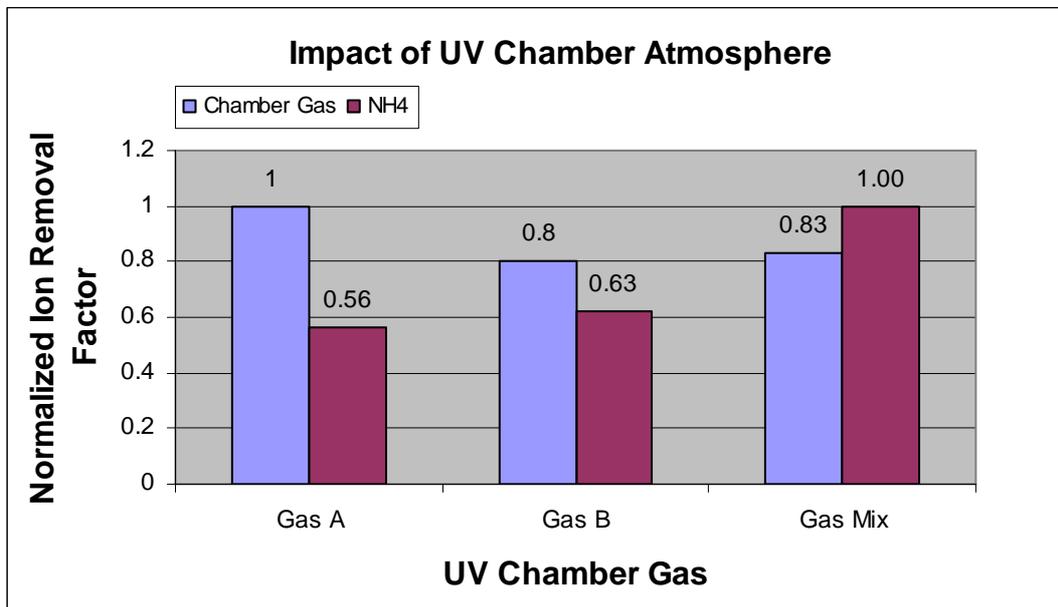

Figure 2: Shows the occurrence of ammonia is higher for a chamber gas mixture which contains constituent elements of ammonia.

UV Gap

The UV Gap refers to the distance between the plate and the excimer lamp housing. Closer Gap distances will increase the energy impacting the plate. Our experiments showed that the closer distance had a strong impact on both sulfate and ammonia ion removals. For sulfate, the 1X Gap was 55% improved over the 3X Gap. For NH4+, the net removal was improved by 73% (Figure 3).
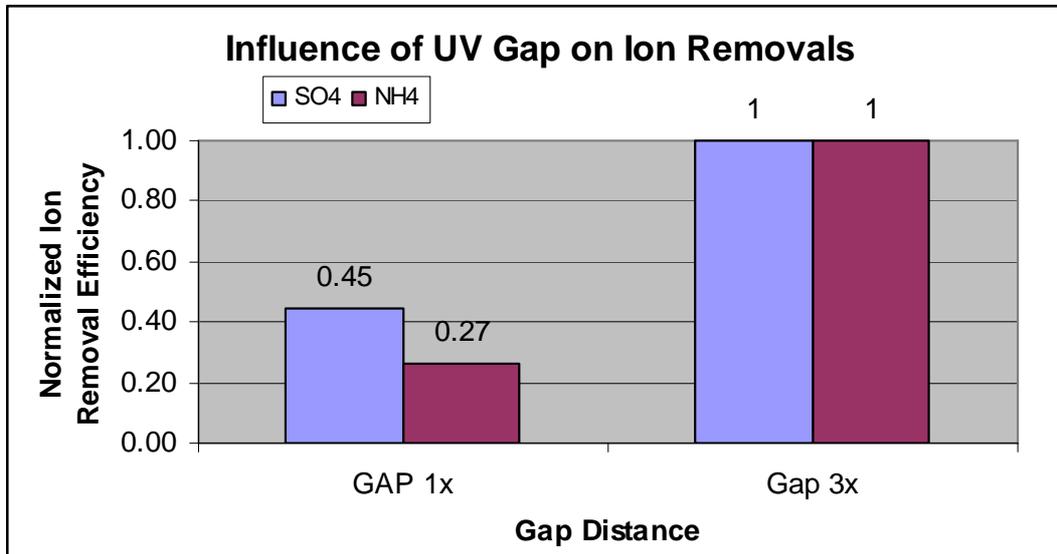

Figure 3: Both ammonium and sulfate are superior for the 1X Gap vs. the 3X Gap in the context of a UV chamber atmosphere containing Gas-Mix.

Bake Duration

Removal sequences which employed a longer bake time showed a 39% improved removal efficiency over the shorter bake time.
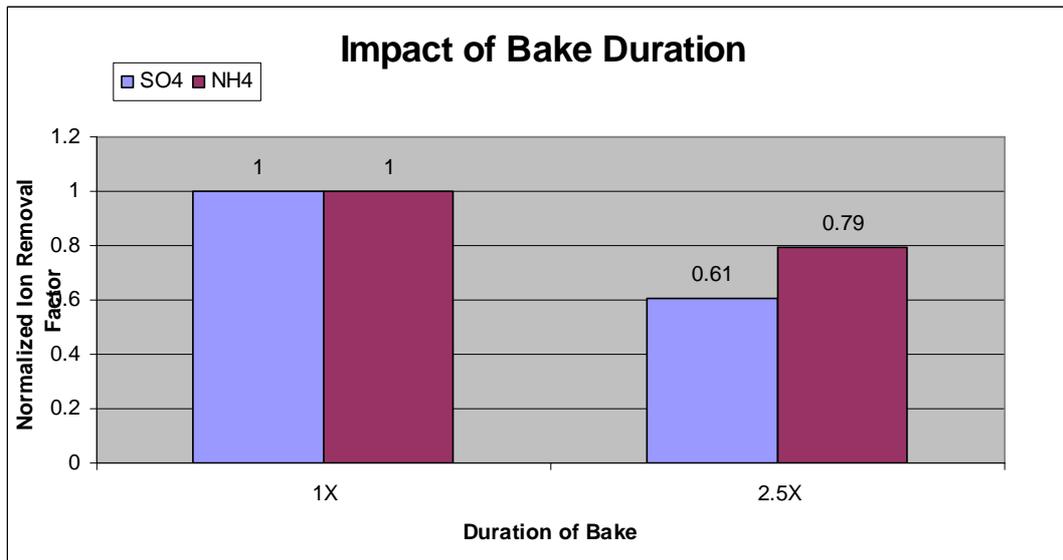

Figure 4: Shows the impact of bake duration tests between 1X and 2.5X favors 2.5X for sulfate and ammonia removal.

The Post UV Sequence

Choosing the right wet process after the UV exposure was important. For sulfate, sequence BA improved removal 55% over sequence AB. Ammonium removal was improved by 27% over sequence AB (Figure 5).
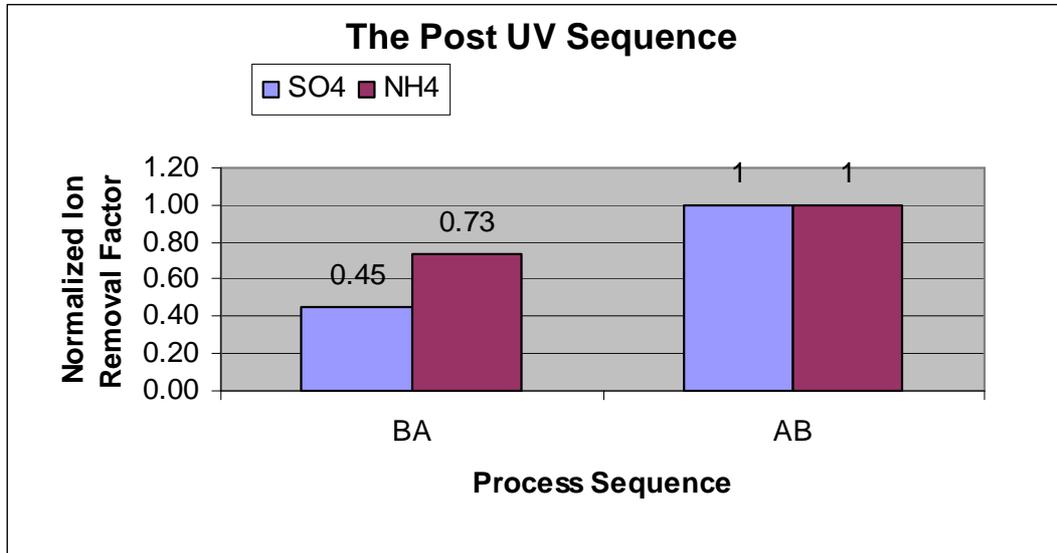

Figure 5: Shows the importance of choosing the right wet process after UV treatment.

Relative Humidity

There are many reports of the relevance of humidity during UV exposure in forming ammonium sulfate. With respect to ion removals, introducing moisture into the UV chamber improved sulfate removal by 18%. Ammonium was improved by only 9% (Figure 6). These levels are close to our experimental noise.
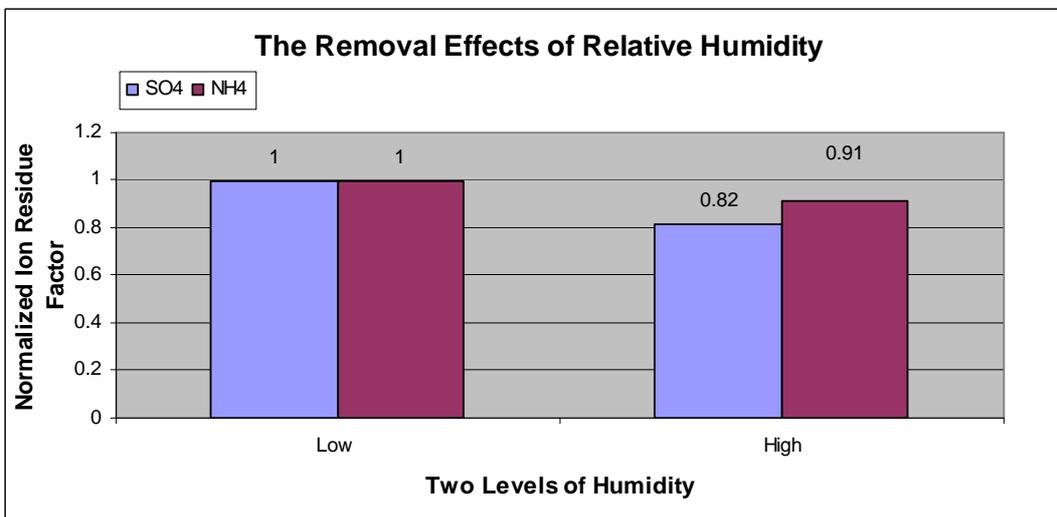

Figure 6: Shows higher RH may be superior to low RH.

Final Sequence

The final steps in our cleaning sequence will impact ammonium much more than sulfate. Figure 7 shows a 31% improvement for the **Dresden Closure** over the **Simple Closure**. Although Figure 7 shows a 13% improvement for sulfate, this result is marginal and could easily be within our experimental noise.
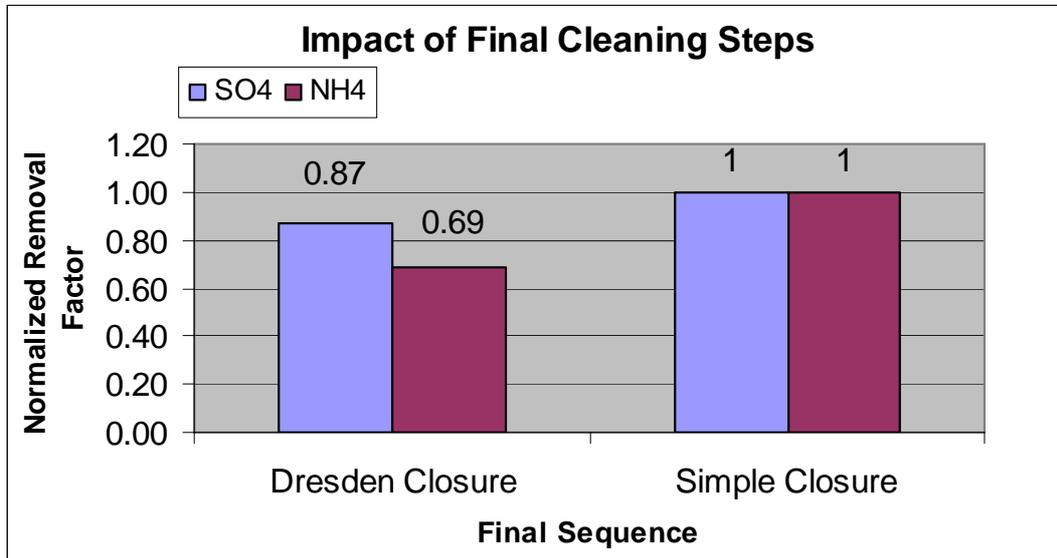

Figure 7: Shows the impact of our final cleaning steps are marginally effective for SO4 but more clearly effective for NH4+.

DISCUSSION

Initial Concentrations on the Photomask

When we apply the principles above, we achieve a maximum sulfate removal efficiency of 87% on a 55 ppb incoming sample, an 84% efficiency for a 25 ppb incoming plate and a 40% efficiency for a 3 ppb plate. The removal coefficient is lower for lower initial concentrations (Figure 8). Based on the removal efficiencies stated above we can anticipate final sulfate and ammonia concentration below 1 ppb on samples of appropriate incoming concentration.

A Work in Progress

Our investigation into room temperature ion removal is a work in progress. Still promising are explorations of UV conditions and subsequent wet cleaning steps. In our sister paper "Mask Cleaning Strategies—Particle Removal with Minimal Surface Damage", we demonstrate room temperature processes with the Phase Angle and Transmissivity figures shown in Table 1. Also shown in Table 1 are the literature values from major mask houses with similar capabilities. We also report a cleaning capability for SiN particles of 99+%. We feel that these simultaneous capabilities will be novel and desirable for the foreseeable future.
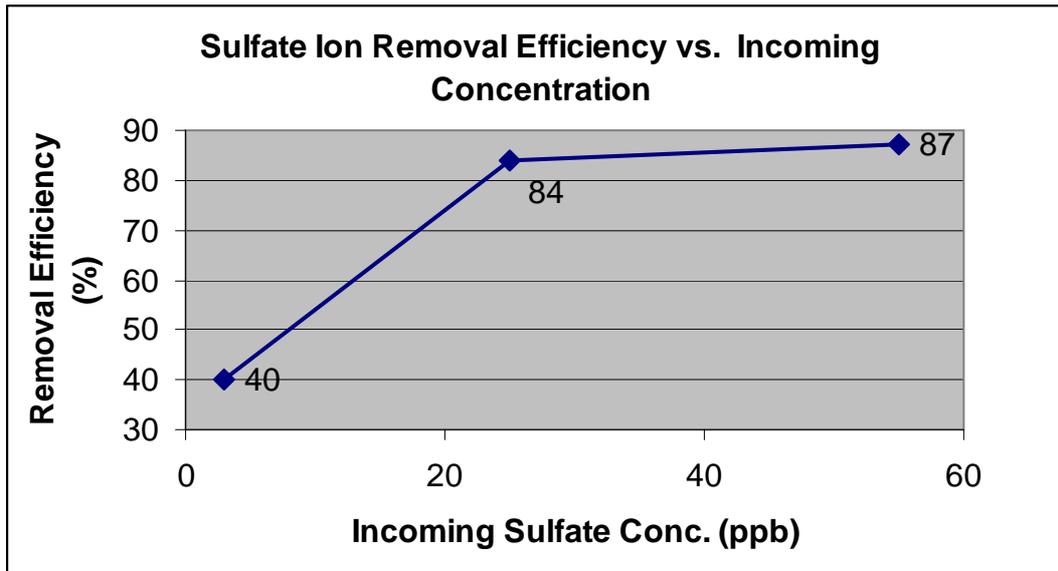

Figure 8: Shows that the removal rate efficiency for sulfate decreases with incoming concentration.

Item	DPI/Akr[5]	DPI/Akr[5]	Top/Mitsu[6]	Sigmameltec MRC3000
Phase Shift deg/clean	*0.07*	*0.7*	*0.1*	*0.065*
Trans Shift %/clean	*-*	*0.05*	*0.02*	*0.016*
Cleaning Conditions	**DIO3/SC1 22C Rinse**	**DIO3/SC1 70C Rinse**	**Bath not Spin**	**Room Temp Spin**

Table 1: Shows world class Phase Shift and Transmissivity figures are possible with 99+% SiN particle removals.

REFERENCES

1. Eric Johnstone, Laurent Dieu, Christian Chovino, Julio Reyes, Dongsung Hong, Prakash Krishnan, Dianna Coburn and Chris Capella, "193 Haze Contamination: A Close Relationship between Mask and its Environment", . Proceedings of 23rd Annual BACUS Symposium on Photomask Technology, SPIE Vol. 5256, p.440-448.

2. Sung-Jae Han, Sang-Yong Yu, Moon-Gyu Sung, Yong-Hoon Kim, Hee-Sun Yoon, Jung-Min Sohn; "The Study on Characteristics and Control of Haze Contamination induced by Photochemical Reaction."; Photomask and Next-Generation Lithography Mask Technology X, SPIE Vol. 5130 (2003), p.563-567.

3. Chia Hwa Shiao, Chien Chung Tsai, Tony Hsu, Steve Tuan, Doris Chang, Richard Chen, Frank Hsieh; "Evaluation, Reduction and Monitoring of Progressive Defects on 193nm Reticles for Low-k1 Process"; Photomask and Next-Generation Lithography Mask Technology XI, SPIE Vol. 5446 (2004), p.225-230.

4. Florence Eschbach, Daniel Tanzil, Mike Kovalchick, Uwe Dietze, Min Liu, Fei Xu; "Improving photomask surface properties through a combination of dry and wet cleaning steps"; Photomask and Next Generation Lithography Mask Technology XI, Proceedings of SPIE Vol. 5446, 2004.

5. Gim Chen, Julio Reyes, James Wood, Ismail Kashkoush, Laurent Dieu, Richard Novak; "Immersion System Process Optimization for 248nm and 193nm Photomasks-Binary and EAPSM"; Proceedings of 23rd Annual Symposium on Photomask Technology; SPIE Vol 5256; p. 518-525.

6 Koji Tange, Yoshikazu Nagamura, Kunihiro Hosono, "The Development of Refined Cleaning Technique Focusing on Ecological Viewpoint", ", Photomask and Next-Generation Lithography Mask Technology VIII, SPIE Vol. 4409 (2001), p.418-429.