

## **193nm Haze Contamination: A Close Relationship between Mask and its Environment**

Eric V. Johnstone\*, Laurent Dieu\*, Christian Chovino\*, Julio Reyes\*  
Dongsung Hong\*\*, Prakash Krishnan\*\*, Dianna Coburn\*\* and Chris Capella\*\*

(\*) DuPont Photomasks Inc., Round Rock, TX

(\*\*) Cypress Semiconductor, Inc., San Jose, CA

### **ABSTRACT**

The integration of 193nm Lithography is close to full production for the 90nm node technology and shows potential for lithographic resolution down to the 65nm node. The quality of 193nm reticles including binary, EAPSM and AAPSM must be outstanding so that low K1 factor reticles may be used in production.

One area of concern in the IC industry is haze contamination on the mask once the reticle has been exposed to ArF radiation. In this study, haze was found outside of the pellicle and on the quartz side of the mask. Standard through-pell inspections might miss the contamination, yet its severity can ultimately affect mask transmission. For this reason, DuPont Photomasks and Cypress joined forces to quickly decipher how it develops.

In this investigation, tests were devised which altered conditions such as mask environment, exposure, traditional and advanced cleaning chemistry. This paper describes the relationship between surface and environmental photochemical reactions, the resultant growth, analysis, and how it is controlled.

Keywords: DUV, mask contamination, 193nm contamination, haze, mask environment, mask clean

### **1. INTRODUCTION**

Until recently, the sole measure of a reticle's cleanliness prior to shipment was its performance at inspection. As mask materials change and exposure wavelengths shrink, the science of cleaning has taken a giant leap forward. Residuals on the surface and in the environment around the mask become more relevant as their byproducts can be fatal to the reticle's performance. Mask makers must now be proactive and find ways to verify the robustness of new materials and carefully assess processes changes. Furthermore, new measures must be devised to forecast problems as newer products unfold.

DPI faced this challenge unexpectedly in 2002 when a growth contamination (haze) was found under the pellicle in two unrelated situations- pre and post exposure on 248nm EAPSM masks. A team was immediately formed and the process dismantled through extensive Design of Experiments. The first order of business was containing the outbreak. However, the difficulty of recreating the problem in a controlled manner quickly became the focus. The root cause ultimately stemmed from a new pellicle material in one case, and a slight change in blank manufacturing in the second. In the end, new mask stressors were added to the matrix of change control protocol used to predict mask failure and provide quality assurance.

In preparing for the ramp up of 193nm products, DPI sought to identify potential roadblocks by surveying the industry. In tandem, a laboratory was set-up with ArF radiation to provide firsthand worst-case feedback; given the uncontrolled environmental and exposure conditions used. Much of the industry had already reported growth beneath the pellicle. Fortunately for DPI, this was not the case. However in our tests, we found a new growth on the glass side of the mask. This was verified in the field through a bright light visual inspection of the backside- and was a surprise to many customers.

An alliance between DPI and Cypress was formed to build on our understanding of the mechanisms that contribute to this effect. In this study, a comprehensive and practical analysis of mask making process variables and real world end-use conditions were evaluated to assist in our discovery of the root cause and in finding the boundary limits controlling this phenomenon on the mask.

## 2. OBSERVATION

Inspection of DPI 193nm reticles used at Cypress was consistent with lab findings. Growth was also found on the chrome side of the mask outside of the pellicle in selective patterned areas. Glass side haze was so far invisible to the process, but concern arose that a seemingly subdued growth left unchecked might ultimately affect mask transmission properties or eventually extend into the pattern itself.

The glass side haze can be described as a fine milky film varying in density and with some color. The film growth and density is directly proportional to cumulative exposure, leaving evidence of 'blades' or blocking within the stepper as witnessed by the mask. (see Figure 1). The growth was reported to occur at a very low energy, sometimes triggered at less than a dozen wafers exposed.

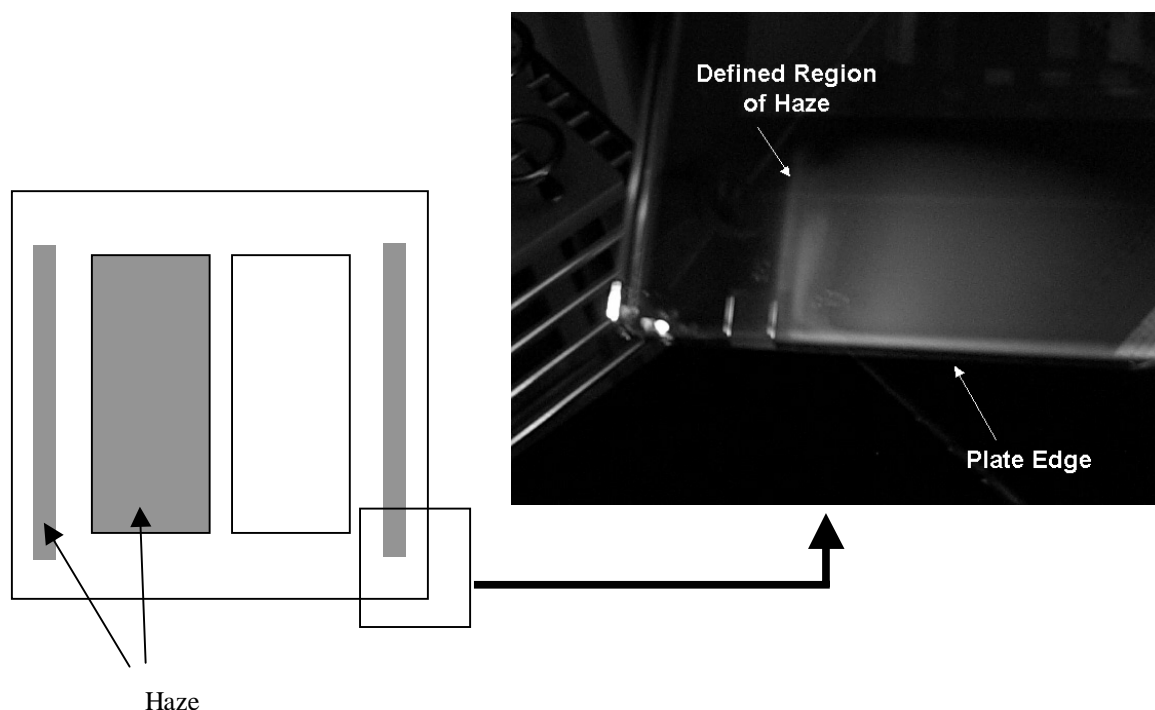


Figure 1 – Map of haze as found on the glass side of a mask. The hazed die and rectangular areas on the edges of the mask were the only areas exposed to 193nm radiation within the litho tool.

Haze found on the chrome side of the mask outside of the pellicle was less dense than glass side haze. Infected areas were limited to clear patterns that were exposed to 193nm radiation (i.e. for alignment purposes) and correlated to the repeated set up of the mask and not the total energy exposed within the patterned area.

193nm mask types used at Cypress were binary and were mounted with dual-band (193nm & 248nm) pellicles. The compact material used in all shipments to Cypress was Bayon- a standard in the industry. At the time of discovery, backside haze on the mask was not reported to have affected the performance at the wafer level. However, CD drift due to contaminated optics in the litho tool was a reported factor, which until recently, was remedied through frequent lens wiping.

### 3. EXPERIMENTAL

#### 3.1 Fab Environment

The exposure of test masks was performed in a laboratory setting designed to mimic a DUV stepper system. In order to accurately reproduce the fab environment (both mask storage and usage conditions), a contracted analysis of the environment within the litho tool at the mask plane and in the ambient area near the tool were performed at Cypress Semiconductor. The analysis included sampling of inorganic materials (including acids and bases) and high boiling point organics. Air samples purged through ultra pure water were set out for a four-hour period and then processed using Ion-Chromatography. A concurrent sampler purged air through a porous collection media and was analyzed using a Gas Chromatograph equipped with a Mass Selective Detector and Thermal Desorption System. Samples were measured against control blanks that used the same collection media and were handled in the same way, but with no volume drawn.

The litho tool was equipped with a dedicated carbon media filter box and fan, drawing fab air and providing positive pressure (~1200 Pa) within the cabinet. During the sampling period, it was noted that the lens system of the litho tool was separately contained and purged from a different source, drawing air from the tool cabinet and then through an additional low volume broad-spectrum type canister filter and at a slightly boosted pressure. Samples within the lens containment could not be taken.

	Concentration						
	ppbv						ug/m <sup>3</sup>
	Ammonia (as NH <sub>4</sub> <sup>+</sup> )	Sulfur Dioxide and Sulfuric Acid (as SO <sub>4</sub> <sup>-2</sup> )	Hydrochloric Acid (as Cl <sup>-</sup> )	Hydrofluoric Acid (as F <sup>-</sup> )	Nitrous Acid (as NO <sub>2</sub> )	Nitric Acid (as NO <sub>3</sub> )	High Boilers
Inside Litho Tool	0.5	<0.1	<0.1	<0.1	1.3	<0.1	140
Fab Ambient	2.6	<0.1	0.1	<0.1	1.5	0.1	406

Table 1. Environmental analysis of the litho tool and ambient within the fab

As can be seen in Table 1, the low concentrations of acids and bases were impressive. Nitrous acid, a weak acid, was markedly higher. Primary players, such as ammonia, were kept at sub 1 ppb within the tool and to exceptionally low levels even in the ambient.

Masks being stored while not in use were transferred from the original single-mask compact used for shipping, to a cassette pod holding as many as six masks. Cassettes, constructed of plastic and aluminum, were stored in the ambient environment of the fab and kept separate from the litho and process areas. Although the cassettes provided physical and particulate protection, only a single ring gasket separated the internal cassette environment from its external environment. Furthermore, there was no mask-to-mask segregation within the cassette, allowing for the possibility of cross contamination. Analysis of the cassette and gasket materials was not performed.

#### 3.2 Laboratory Set-Up

Optical variables adjusted in the lab - including laser fluence & frequency, temperature and pressure – were matched to litho tool specifications and tested initially using a similar environment to that of the measured litho tool.

Afterwards, variables were manipulated so that testing could be accelerated while still providing an accurate response as compared to examined masks in the field. This was verified through quantitative and qualitative analyses of mask surfaces in addition to tool and visual inspections. Haze produced in the lab varied only by grain size, yielding a slightly courser contamination. These adjustments enabled feedback times of less than three days per test exposure.

Additionally, the lab setting allowed the use of instrumentation and environmental controls that would not otherwise be feasible or possible in a wafer fab. This included an elaborate mask chamber with flow directional baffles, gas dispensing and chemical monitoring. (Figure 2)

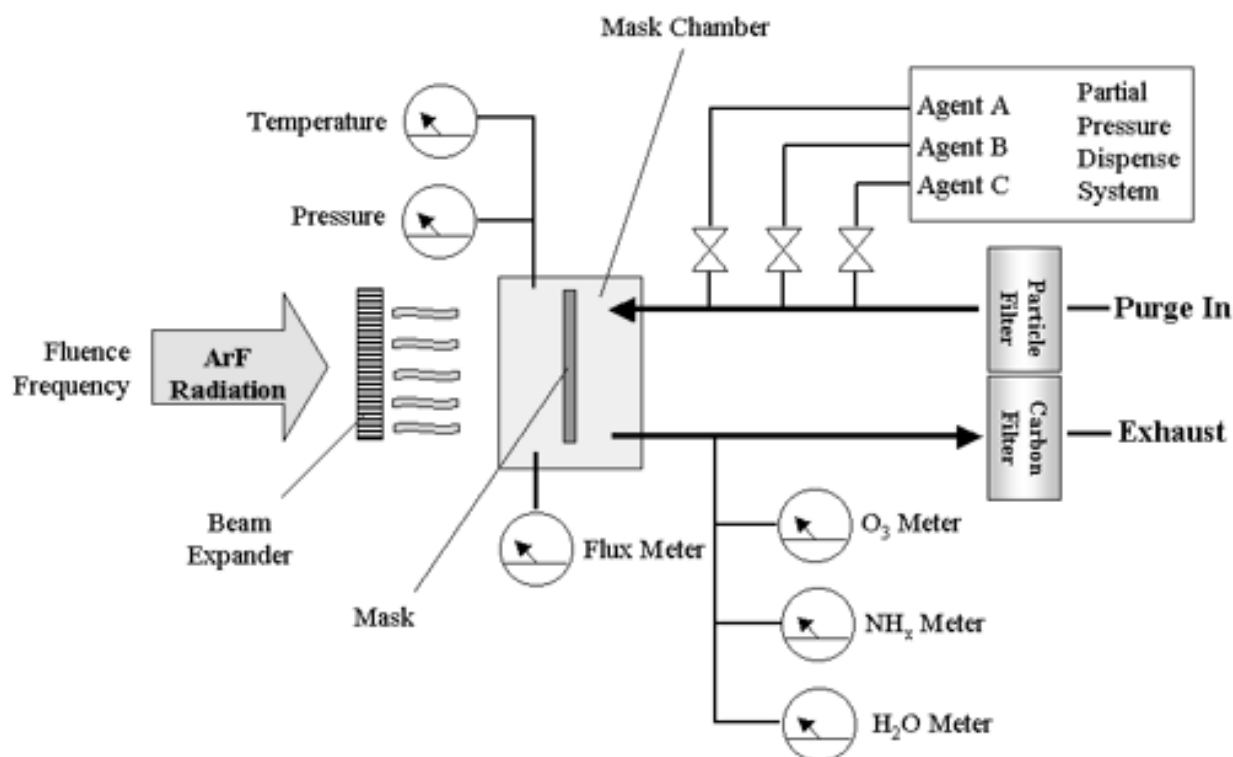


Figure 2 – Laboratory Setup of Test Exposure System

### 3.3 Contamination Analysis

An outsourced lab using Raman Spectroscopy and Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) performed analysis of the haze. Multiple analyses pointed to Ammonium Sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) as the leading constituent (Figure 3). This was referenced against a control mask that was not exposed. Cyanuric acid was not detected, contrary to previous studies that found haze growth at 193nm within the patterned area under the pellicle<sup>1</sup>. The analysis also ruled out another potential key player, organic airborne molecular contamination, which is also believed to contribute to hazing through condensation and adsorption<sup>2</sup>.

The formation of salts at shorter wavelengths due to available anions and cations has been well documented within the IC industry. The main focus of many campaigns within the mask world has been to drive to new levels of cleanliness to ward off such a reaction. Having found airborne levels of ammonium (as NH<sub>4</sub><sup>+</sup>) and sulfates (as SO<sub>4</sub><sup>-2</sup>) at the point of use, the next task was to find where these ingredients resided and what levels were permissible.

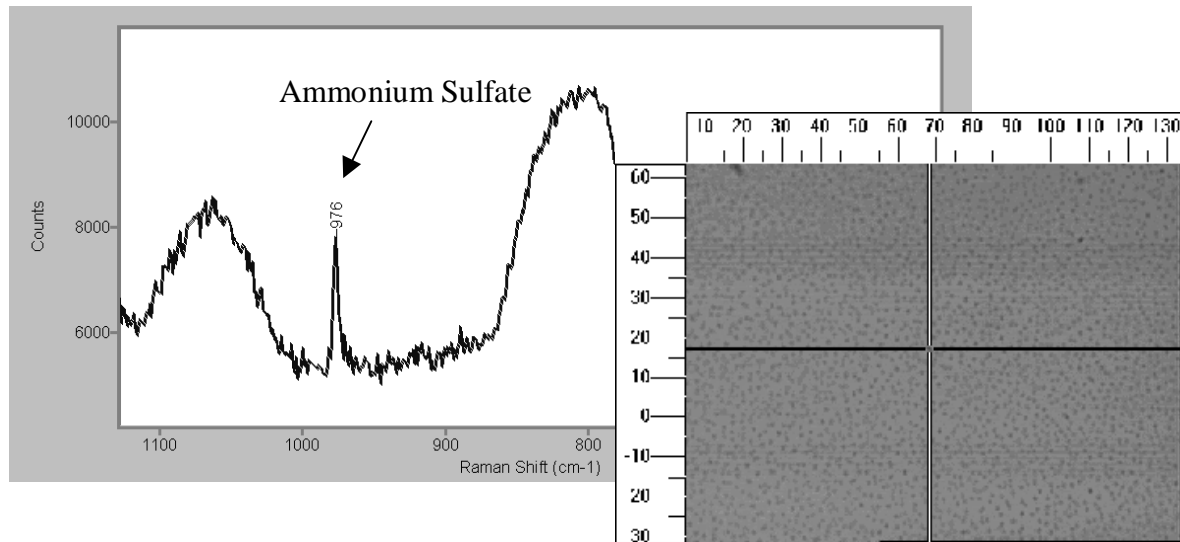


Figure 3- Raman spectra of backside contamination and scope view showing density of growth

### 3.4 Experimental Matrix & Results

A detailed array of mask manufacturing parameters was assembled for testing to determine which components were linked to the contamination (Table 2). This was derived from a commonality study which cross examined process and clean chemistries among products, mask blank materials, optical platform and resist, pellicle type and compact materials. Exposure environment was a coupled variable controlled at the lab. All combinations were exposed from the backside of the mask using a total energy of 2.5 kJ, a level found to be a reliable predictor of long-term haze growth.

Surface cleans evaluated were specific to 248nm reticles, and were proven to be the best cleans through extensive laser durability tests and particulate removal efficacy (**Clean A**). Through the use of Ion Chromatography (using full immersion extraction of residuals on the surfaces of the mask), this correlated to sulfate levels of 15 ppb and ammonium ions level of 4 ppb. Control blanks (**Clean B**) were prepared using virgin mask blanks immersed in hot DI water for 15 minutes. This was measured similarly to have sulfate and ammonium levels of 3 ppb. The control masks were not inspected for particles on the surface.

Pellicle and compact materials were also of interest, as recent literature has pointed toward their possible affiliation with 193nm haze<sup>1</sup>. The pellicles used on masks evaluated at Cypress were dual band 193nm & 248nm films. For this test we used the same, and additionally included a single band 193nm Cytop film and a control with no pellicle. Compact materials included Bayon, a DPI standard, and polycarbonate + carbon which is known to outgas less.

The environment within the mask chamber was controlled using a base purge of bottled clean & dry air with less than detectable levels of sulfates and total amines (**Environment A**). The make-up of contaminated air contained levels of sulfates in the range of 8-10 ppb and total amines of 15-20 ppb (**Environment B**). This was controlled using a separate dispense system within the same chamber. Between test exposures, the chamber was disassembled and wiped down with IPA to avoid cross contamination issues.

1st Group

<i>E-Beam</i>			<i>Laser</i>		
<i>Resist A</i>	<i>Resist B</i>	<i>Resist C</i>	<i>Resist A</i>	<i>Resist B</i>	<i>Resist C</i>
<i>Clean A</i>	<i>Clean B</i>	<i>Clean A</i>	<i>Clean B</i>	<i>Clean A</i>	<i>Clean B</i>
<i>Env B</i>	<i>Env B</i>	<i>Env B</i>	<i>Env B</i>	<i>Env B</i>	<i>Env B</i>
<i>Clean A</i>	<i>Clean B</i>	<i>Clean A</i>	<i>Clean B</i>	<i>Clean A</i>	<i>Clean B</i>
<i>Env A</i>	<i>Env A</i>	<i>Env A</i>	<i>Env A</i>	<i>Env A</i>	<i>Env A</i>

**Variables**

*Process*  
*Resist Platform*  
*Clean*  
*Environment (Env)*

**Controlled**

*Blank Material (Binary)*  
*Pellicle Supplier (Pell A)*  
*Compact Material (Bayon)*

*Clean A* = *Current Clean*  
*Clean B* = *Control (Best Clean)*

*Env A* = *Control (Best Environment)*  
*Env B* = *Contaminated*

*Pell A* = *Cytop Single Band*  
*Pell B* = *Cytop Dual Band*

**Exposure Conditions:**

*ArF ( 193 nm )*  
*2.5 kJ Total Energy*

2nd Group

<i>Bayon</i>			<i>PolyCarbonate + Carbon</i>		
<i>Pell A</i>	<i>Pell B</i>	<i>No Pell</i>	<i>Pell A</i>	<i>Pell B</i>	<i>No Pell</i>
<i>Binary</i>	<i>Binary</i>	<i>Binary</i>	<i>Binary</i>	<i>Binary</i>	<i>Binary</i>
<i>EAPSM</i>	<i>EAPSM</i>	<i>EAPSM</i>	<i>EAPSM</i>	<i>EAPSM</i>	<i>EAPSM</i>

**Variables**

*Compact Material*  
*Pellicle Supplier*  
*Blank Material*

**Controlled**

*Process (Laser)*  
*Clean (Clean B)*  
*Environment (Env A)*  
*Resist (Resist A)*

 *BACKSIDE HAZE*  
 *NO BACKSIDE HAZE*

Table 2 – Summarized matrix of test variables and results. Variables found not to haze within Group 1 (Clean B and Env A) were carried over to test variables within Group 2.

The results confirmed the two variables in question – cleaning residuals and environmental contamination – as both playing a role in contributing to the salt formation on the backside of the mask. Other variables were discounted, such as pellicles and compact material.

In a follow up experiment, the variables were separated to demonstrate the effects of each. Purge baffles within the exposure chamber were directed over only one half of the mask to localize airborne contamination. Four masks were exposed using the different combinations of cleans and environments.

The effects of each were visibly evident- poor cleaning left an obvious radial pattern around the perimeter of the mask, and the redirected airflow highlighted the effects of environmental contamination. Most importantly, the experiment highlighted the independence of each as a mechanism for creating the growth.

Figure 4 illustrates the pattern of haze formed. In a final test, the rinse was eliminated from a spin clean process to create a surface extremely high in sulfates and ammonium residuals (Bad Clean). Results are shown in the accompanying photograph.

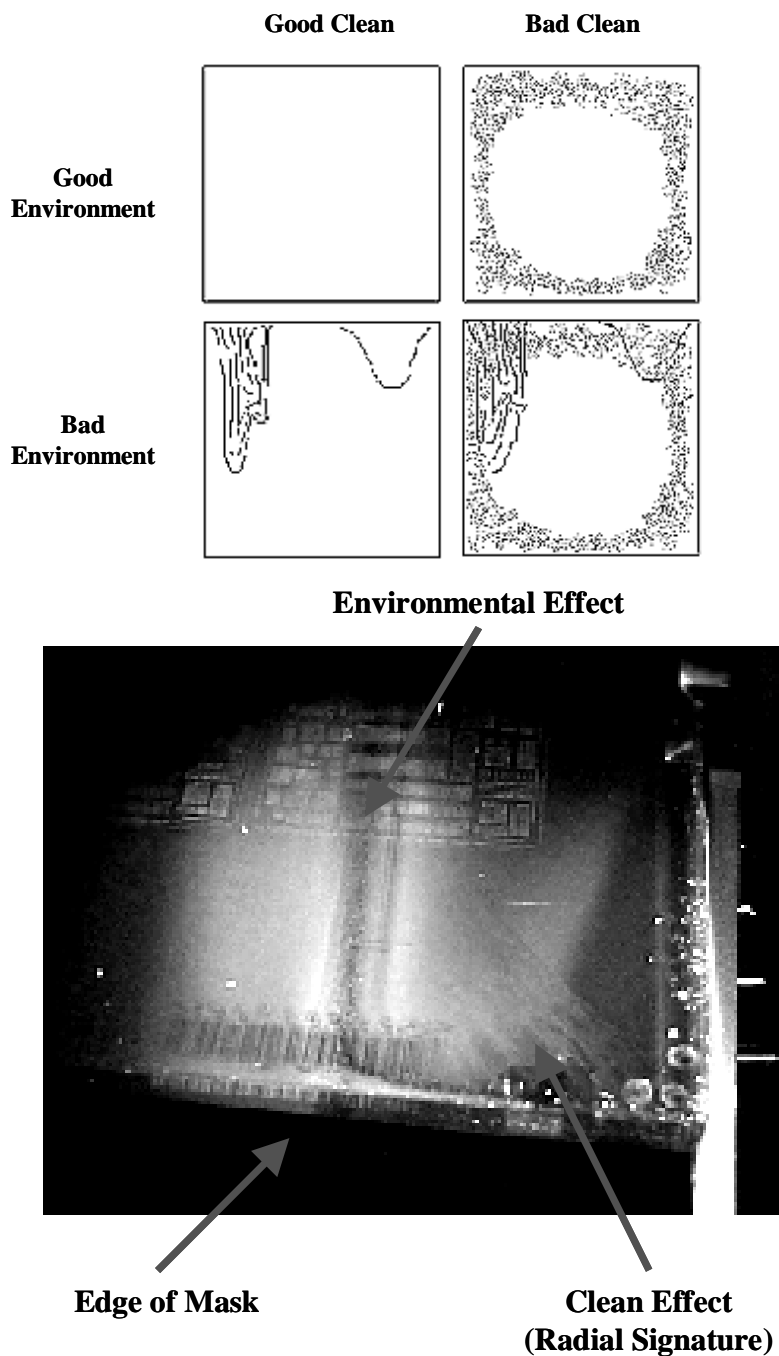


Figure 4. Growth patterns resulting from exaggerated cleans and environmental conditions (above) and photo of the extreme case (below).

## 4. DISCUSSION & CONCLUSION

Results from the matrix of experiments validated the following:

- Environmental photochemical reaction at 193nm - compounds in the environment near the exposed mask, combine and migrate to the surface
- Surface photochemical reaction at 193nm - residual chemistry left on the surface after a clean will combine on the surface

The experiments also underscored the additive effects of each, which further defined the relationship between exposure energy and residuals present required to form the salt. The two components in our case, ammonium ( $\text{NH}_4^+$ ) and sulfates ( $\text{SO}_4^{2-}$ ), are commonly found in mask cleaning chemistries and also within the environment. In this experiment, we were able to prevent haze growth by reducing contaminant levels on both the mask and within the environment when exposed to a total energy equaling 2.5 kJ. Since this energy level was used to reproduce the effects only, and did not represent real-world usage of a mask in the fab, the specifications for both environment and surface residual levels had to be more stringent. To fulfill the role of a responsible mask supplier, DPI targeted 5kJ as a total energy haze-free goal as measured within a clean environment and confronted the task of developing new cleaning strategies to reach this point.

Understanding the complete neutralization of chemistries and how surface compounds coexisted post-clean was key in reducing residuals to barely traceable levels. In follow up experiments, sulfate and ammonium concentrations were purposely elevated in different ratios to study the affiliation of cross contamination within a contained and measured environment. The results showed volatile ammonium in the air - even in trace amounts - was drawn to sulfates on the surface, however the reverse was not true. This underlined the fact that sulfates are the dominant variable in measuring a clean. It also suggests that mask-to-mask contamination is not likely an issue until masks are one day used and stored in a near perfect environment.

In another study, we examined the distribution of residuals on the mask surface. Levels measured along the outside edge of the mask were nearly double in concentration as compared to the center region. Furthermore, the spatial mapping of higher concentrated areas on the chrome side correlated well to areas that were prone to hazing from radiation during alignment. This feedback enabled us to develop a more effective and balanced cleaning process on glass and chrome, extending clean levels found within the critical areas beneath the pellicle to the mask edge.

Capping the backside of the mask is a DPI patent-pending approach to eliminating all surface residuals by replacing the surface. Using a spin technique, this process was demonstrated using a fluoropolymer film applied to the backside of the mask as a final step before exposure. The thickness was tuned to maximize transmission and the material properties provided additional optical benefits. Test plates proved to be haze free, although there is still much to evaluate before this becomes a viable production option.

Ultimately, the lower limits of sulfates necessary to prevent haze from forming at a 5 kJ total energy was found to be sub 1 ppb - chrome and glass side combined. This was demonstrated on a test mask using an experimental clean process and exposed under ideal conditions (zero sulfates). Second level testing is in place to evaluate a production run using these conditions and results have yet to be confirmed at a customer site.

As a manufacturer of 193nm photomasks, DPI is accountable for its role in preventing haze by providing a superior mask surface. Likewise, the counter role of litho tool manufacturers is to ensure a pristine environment. In our laboratory set-up, we were able to measure our own performance within an ideal environment to reach proven ground- a 193nm haze free mask exposed at a total energy of 5kJ. Thanks to determination and an open relationship between supplier and customer, the reactions were properly dismantled and a new cleaning standard was established for the upcoming generation of photomasks.

## REFERENCES

1. K. Bhattacharyya, W. Volk, B. Grenon, D. Brown, J. Ayala, "Investigation of reticle defect formation at DUV lithography", BACUS 2002
2. A.J. Dallas, D. Arends, K. Fischer, J. Joriman, K. Graham, R. Ringold, "Protecting the DUV Process and Optimizing Optical Transmission", Metrology, Inspection, and Process Control for Microlithography XIV, Volume 3998 (2000)