# A practical solution to the critical problem of 193 nm reticle haze

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## ABSTRACT

The authors have developed and successfully implemented a practical, yet effective solution to help eliminate haze formation in the production fab. Based on a novel mechanism of haze formation described earlier, along with a thorough understanding of the reticle surface chemistry changes during the manufacturing process, the authors found an unexpectedly simple and straightforward way to prevent haze formation. This is possible regardless of the origin of the reticle, by controlling the purity of the immediate reticle environment.

yield improvement, optics contamination control, haze formation, XCDA, ammonium sulfate crystal growth

## 1. INTRODUCTION

In previous papers [1, 2] the authors outlined the mechanisms of reticle haze formation of different chemistries and provided the theoretical basis for a practical solution to it's formation in an IC manufacturing environment.

This article presents successful results of reticle protection solutions implemented at a major IC manufacturing facility and provides practical recommendations for implementing the proposed reticle haze solution.

Because reticle haze control and reduction enables yield improvement, it presents a serious and vital issue of competitive advantage for IC manufacturers. As a result, we are not always at liberty to discuss many of the specific or sensitive details of successful implementations of the proposed solution. Readers are advised to keep in mind that statements made in this paper seemingly without supporting data and/or significantly detailed discussion are not general considerations, but rather, are the result of such confidentiality limitations.

## 2. OVERVIEW OF RETICLE HAZE MECHANISM FORMATION

In [1] the authors explained that reticles are fundamentally more susceptible to haze formation than exposure tool optics. We consider reticles as being another (removable) optical element in the scanner. The reticle has four optical surfaces (counting the pellicle) and is exposed to the same dose of UV light in the same mini-environment as other permanent optical elements in the reticle stage free working area. Yet, reticle haze occurs much more frequently and severely on the reticle than on the optics. With more than 15 years of experience working with UV optics contamination control, we believe that understanding the detailed causes of this discrepancy is key to pinpointing the root cause of reticle haze and to developing an efficient solution to control it.

From a chemical contamination standpoint, we identify three major differences between a reticle and a scanner lens:

1. Materials of construction (surface chemistry)
2. Presence of the pellicle
3. Stability of the atmospheric environment.

The difference in construction materials or surface chemistry has the greatest effect on the reticles' susceptibility to haze growth. This is due to the chemical modification of the quartz (hydration of quartz) and chrome (formation of chromium sulfate) surfaces during the reticle manufacturing process. Recent changes to cleaning procedures to reduce haze formation may not fix the problem at all. Rather, it essentially shifts the chemistry of the haze. Eliminating ammonium and sulfuric acid from cleaning procedures for example, might reduce the ammonium sulfate haze, however, what we then see, is an alternative haze formation mechanism. There are multiple new reports [4] on growing instances of oxalate haze, which we attribute to the changes in the cleaning procedures during reticle manufacturing.

Ammonium sulfate haze formation mechanism is described in Figure 1.

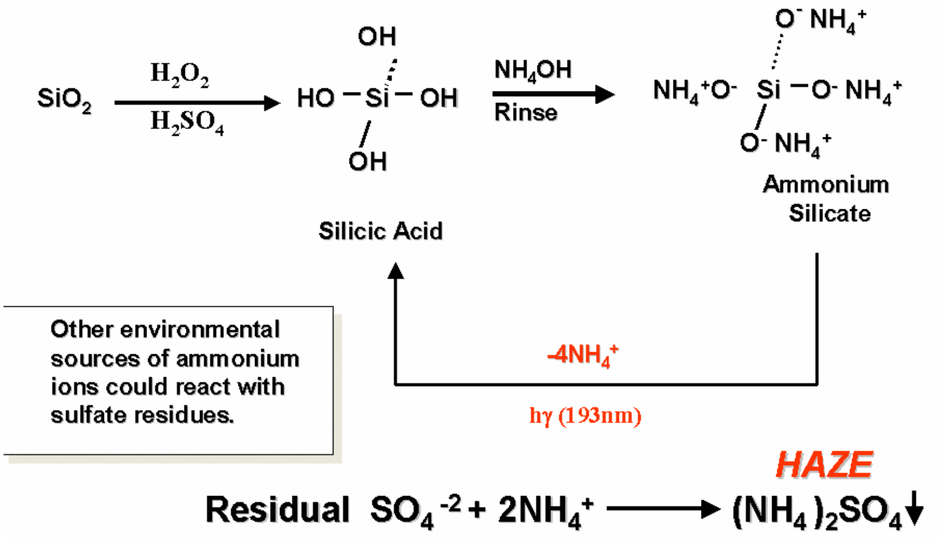

Figure 1. Cycle of ammoniumsulfate haze formation. Ammonium comes from the ammonium hydroxide rinse (and possibly from environmental sources of ammonia). Sulfate comes from the cleaning process and from the environmental sources of $SO_2$. It rides on the chrome surface as $Cr_2$ $(SO_4)3$* $nH_2O$. UV light in the presence of water mobilizes contaminants, and the sub-pellicle space provides a perfect photochemical reactor.

It may also be noted that the presence of certain amounts of water in the form of the moisture in the sub-pellicle space is an important factor in triggering this mechanism. Removing water from the sub-pellicle space will interrupt, thereby preventing photo-induced growth of ammonium sulfate crystals.  Water may be removed by storing reticles in an environment with a very low level of humidity. The exact level of humidity which provides reticle protection is yet to be determined. However, some studies [4] indicate that that typical "house" CDA with ~ 2000 ppb of moisture is *not* dry enough to interrupt haze formation. However, purge gas with < 1 ppb of moisture does seem to provide sufficient haze protection.

Photochemical mechanisms for formation of haze other then ammonium sulfates are described in [2] and illustrated in Figure 2. All discussed mechanisms include water as a necessary re-agent. As in the case of ammonium sulfate haze, haze of alternative chemistries may be effectively prevented by maintaining a sufficiently low humidity level in the sub-pellicle space.

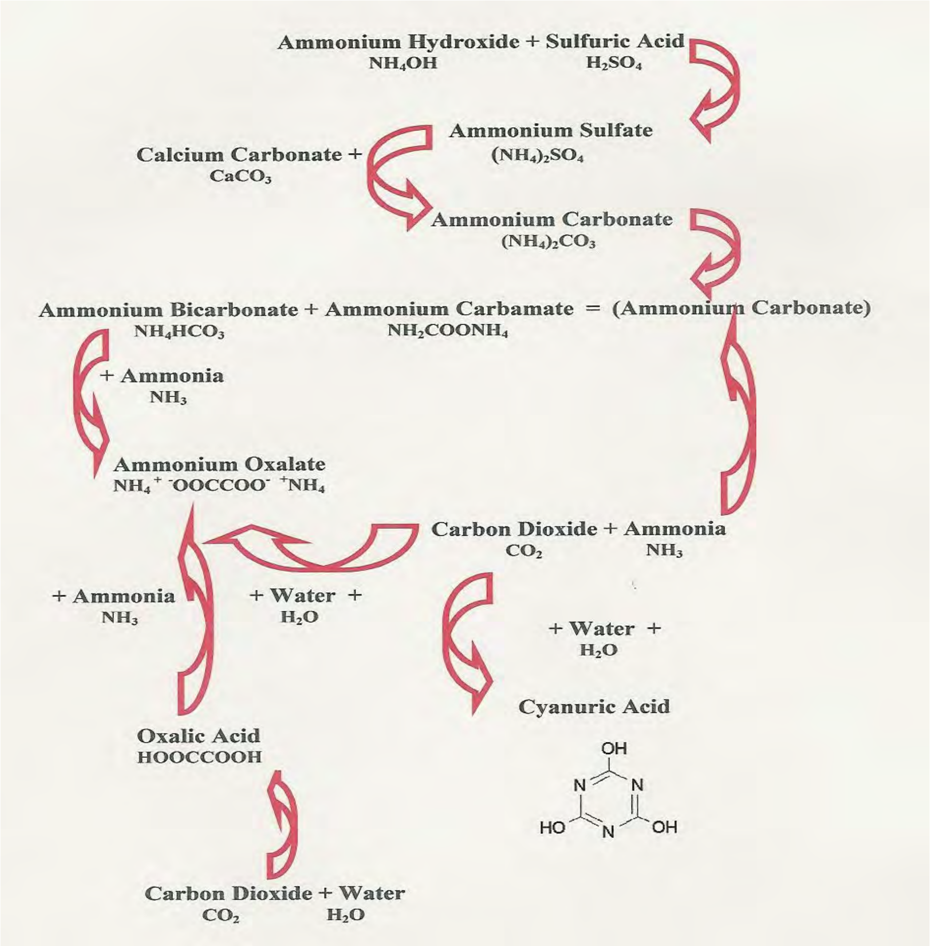

Figure 2. Varying chemical reactions potentially leading to haze formation. (Adopted from B. Grenon et al [2])

## 3. A SOLUTION TO RETICLE HAZE

Our proposed and proven solution to reticle haze suggests keeping reticles in a chemically-purified dry environment from the moment of arrival at the production fab and throughout its useful life. This is achieved by providing a continuous purge with chemically purified gas while the reticle is in storage and being used. This continuous exposure to chemically purified gas is then continued during transport using a purifier. In addition to being free from the regular set of impurities specified for optics protective purge- A-acids, B-bases and C-condensable organics, the typical set of pollutants for optics protection, reticle purge gas should be sufficiently moisture free.

The exact limits of humidity which provide adequate haze protection are yet to be determined and are currently being studied. Preliminary data indicates that purging with the boiled-off nitrogen of chemically purified CDA (XCDA) is adequate.[4] Table 1 includes the purities of purge gas (XCDA) delivered by the authors to the reticle enclosures to prevent reticle ammonium sulfate haze formation.

| **CONTAMINANTS** | **XCDA** |
|---|---|
| $SO_2$ | < 1 ppt |
| $H_2S$ | < 1ppt |
| $H_2O$ | < 1ppb |
| $CO_2$ | 5 ppb |
| $NH_3$ | < 10 ppt |
| SILOXANES | < 1 ppt |
| AMINES | < 10 ppt |
| Hydrocarbons | 1 ppt |

Table 1: Contamination level in chemically purified CDA (XCDA)

### 3.1 Purification to parts per trillion

Validating XCDA purifier performance to part per trillion levels is quite challenging. In order to detect these low levels of impurities, a special analytical system was developed. It is a cryo-focused GC-FID and GC-PFPD [5] with an integrated double dilution manifold for generating ppt level calibration standards. But, developing this analytical instrument is only part of the difficulty in measuring these low-level impurities.

Selection of materials for the manifold, valves, tubing, flow controllers, seals, etc. is critically important because they can significantly affect purge times for background gas analysis. The components selected can also lead to “virtual” sources of contamination, much like an internal weld can be a “virtual leak” in an ultra-high vacuum system.

Figure 1 shows hydrocarbon dry-down from an MFC after a ppm level challenge of hydrocarbons. One can see that after seven days of purging, there is still 0.1 to 1 ppb of the impurities that were introduced at 10 ppm and ca. 50 ppb for the toluene impurity introduced at 750 ppm.

Additionally, Figure 2 shows that $SO_2$ takes 24 hours to purge to less than 10 ppt using nitrogen from a stainless steel gas line after a 5 ppm exposure. The graph also illustrates that the $SO_2$ challenge gas cannot be purged to less than 100 ppt using XCDA. These sources of trace impurities require one to carefully select the materials to construct the calibration and testing manifold.

Entegris has more than five years of experience analyzing gases at part per trillion levels for hydrocarbons and sulfur dioxide. We have worked through the difficulties in generating and delivering these low levels of impurities and have developed proprietary methods to measure at these ultra trace impurity levels in reproducible ways. (See Figure 3.)

Figure 3. Transportable analytical set-up for qualifying purge gas quality achieves part per trillion level sensitivity.

The system is built on a cart so it can be transported to field sites for on-site validation of purification systems. Measurements of these trace levels cannot be done with traditional tenax tubes and impinger sampling, which typically have LDL's of 100 ppt. additionally, our experience has shown that these sampling techniques are subject to corruption by atmospheric contamination in the sampling environment and sampling manifold.

### 3.2 Purge gas selection

For practical purposes, purge gases are limited to $N_2$ and XCDA. Noble inert gases (He, Ar) can provide adequate reticle protection, but may be cost prohibitive. The cost of nitrogen relative to XCDA depends on the geographic region and the facility itself. Cost comparisons vary- from XCDA being four times less expensive than nitrogen to nitrogen being slightly less expensive than XCDA. When choosing between $N_2$ and XCDA, it is very important for one to consider not only cost, but also the purity of the nitrogen available at point of use (additional purification and/or periodic purity analysis may add significantly to the cost). In addition another complication relative to using nitrogen purge is its potential health hazard. It is well known in the industry that breathing air enriched with nitrogen, and therefore depleted of oxygen, may lead to severe consequences. (See Table 1) [6, 7] addressing this issue may require specials provisions with corresponding increases in project costs.

| Atmospheric $O_2$ Concentration (%) | Possible Results |
|---|---|
| 20.9 | Normal |
| 19.0 | Some unnoticeable adverse physiological effects |
| 16.0 | Increased pulse and breathing rate, impaired thinking and attention, reduced coordination |
| 14.0 | Abnormal fatigue upon exertion, emotional upset, faulty coordination, poor judgment |
| 12.5 | Very poor judgment and coordination, impaired respiration that may cause permanent heart damage, nausea and vomiting |
| <10 | Inability to move, loss of consciousness, convulsions, death |

Table 2. Health effects of breathing air low in oxygen [7]

### 3.3 The purging process

It is important to purge in every location where the reticle resides, even if only for a short time; these include the scanner reticle storage, reticle stocker, and reticle inspection tools and transport containers.

### 3.4 Scanner

Inside the scanner, the reticle resides either on the reticle stage or in the reticle storage device. Tools that purge the reticle stage with XCDA (or $N_2$) have an intrinsic advantage over the tools that maintain the reticle stage at cleanroom humidity level. This advantage is an overall reduction in relative humidity which eliminates one of the primary catalysts for reticle haze creation. As a result, dry gas purge of the reticle stage is essentially a standard feature on the latest tools.

The same may be said about the purge of the reticle storage device. IC makers who implemented custom XCDA purge in their exposure tools reticle storage mechanisms have seen immediate improvement in their reticle haze situations. [3] Similarly, we anticipate this benefit will create significant demand and that tool manufacturers will ultimately incorporate this feature as a standard on next generation tools as well.

It is interesting to note that when such exposure tools become available, memory chip manufacturers may benefit more than logic chip manufacturers. A memory chip mask set contains fewer critical layer masks then a logic chip mask set. If the reticle storage device has enough capacity to accommodate the entire critical mask set, then permanently storing reticles in the device will provide necessary protection from the haze growth and eliminate the need for an XCDA purged reticle stocker.

Without XCDA purge however, the reticle storage environment does not provide adequate protection. When two identical reticles were stored after exposure to UV light, one in the reticle storage device at ~ 40% RH and the other in the XCDA purged reticle pod, the former reticle had a 100 times higher rate of haze defect growth.[3]

### 3.5 Reticle stocker

Purging a reticle stocker with hundreds of reticles may present certain engineering challenges and warrant cooperation between the manufacturer of the stocker and the supplier of the purge equipment (including purgeable reticle pods).

If a stocker is designed to store reticles in pods, both plumbing and purge port interfaces must be installed. Additionally, certain provisions must be made to ensure:

- Suitable plumbing materials and components are used. (high purity, low moisture permeability, no grease or other off-gassing materials)
- Uniform and consistent flow of purge gas is delivered to each of the hundreds of reticle pods
- The final quality of purge gas delivered to the pods meets stringent requirements. (The authors plan to submit a corresponding article documenting this finding for proposed publication at SPIE Microlithography 2008, detailing the successful conversion of a commercial reticle stocker to a fully purged XCDA version.)

If it is a bare reticle stocker, the situation is different. There is no need for expansive plumbing and purge port installation, however, the amount of purge gas required may be higher than when reticle pods are used.

### 3.6 Reticle inspection tool

Protecting reticles from moisture during inspection should include protection during the actual inspection, as well as while it is waiting for the batch inspection process. The former may be very challenging while the latter is much easier to achieve. In fact, it may not even be possible to purge the inspection tool with extreme dry gas. Unlike scanner DUV optics, inspection tools' optics are designed to operate at different wavelengths. As the result, antireflective coatings on inspection tools optics are much more complex and may be sensitive to humidity variations. This downside is partially off-set by the relatively short duration of the inspection procedure.

In the batch inspection process, reticles may be in the waiting zone for a much longer time than they are in the actual inspection tool. It may be critical to purge the reticle container with XCDA during this waiting period. While not yet a common practice, compact purge stations capable of accommodating up to 10 reticle pods are now available (See below).[8]

There is interesting data to support the need for purging within the reticle inspection phase. In multiple field studies to demonstrate and quantify the success of our approach to reticle haze control, we observed a direct correlation between the frequency of the reticle inspection and the rate of haze defect formation. In all cases, reticles were stored in the XCDA-purged environment and customers implemented batch reticle inspection with the cumulative time of exposure to ambient humidity ranging between 60 minutes and five hours. Detailed reports of this study are scheduled to be published elsewhere.

### 3.7 Transport containers

Reticles are especially vulnerable during transit from one purged location to the next. To reduce exposure to moisture during transit, a two-fold approach may be used.

First, actual transit time should be minimized. In many cases, use of intermediate purge stations may be warranted. Some such stations are only recently available on the market, providing the capability of purging multiple pods. (See Picture 1)

Second, the infiltration of moisture into the pod which is used to transport a reticle must also be reduced. Moisture may enter the pod by either or both of the following mechanisms:

1. Diffusion through existing openings (including around the door seal – pod is not hermitically sealed)
2. Permeation through actual materials of construction.

Our tests of commercial reticle pods showed a diffusion infiltration rate of 10-15 cc/min of in-flowing ambient air. This makes it clear that even a short interruption of the purge flow will lead to fast build up of ambient impurity concentration, including moisture, inside the pod.

We addressed this issue by placing a purifier inside the pod which is capable of adsorbing different classes of impurities, including moisture. In [1] we reported significant improvements of air purity inside the pod equipped with the purifier when purge flow stopped. When purge flow resumes, the purifier is regenerated, restoring its capacity for moisture. The moisture-absorbing capacity of the purifier is limited, however, and it provides only short term (~ 5 – 15 min) protection from moisture infiltration.

## 3. FIELD IMPLEMENTAION OF THE RETICLE HAZE SOLUTION

This solution was practically implemented in the HVM fab of Inotera, a memory chip maker in Taiwan. The exact technical account of this joint work will be published elsewhere. In short, the project had two key goals:

1. Install the practical solution for an existing haze problem in a real-time and real-production environment.
2. Compare this solution to some proposed alternatives.

Our desired target at the start of the test was to have 25,000, 300 mm wafers printed before the printable haze defects developed on the critical layer mask.

To maximize the positive results of the project, we purged with XCDA at all locations where reticles resided for considerable amounts of time. (We are not currently at liberty to discuss the make and model of the exposure tool or the modifications made to it.) Since the reticle was well-protected inside the exposure tool, our main focus was protecting the reticle when it was outside of the tool.

With no purgeable reticle stocker available, reticles were stored in purgeable reticle pods in the individual purge stations in the vicinity of the exposure tool. New generations of reticle pods equipped with internal purifiers and desiccants were used to protect reticles from the clean room moisture while in transit between purged locations. (See Picture 2).

XCDA (see Table 1) was used in our design for purging the reticle at all selected purge locations, both outside and inside the exposure tool.

The alternative protection scheme of compressed house nitrogen was used to purge the reticle pod environment (no purge though the reticle pod).

In addition, to better understand the degree of environmental protection required for reliable reticle haze prevention, several purge tests were run outside the exposure tool:

1. Control: No purging. Environment at clean room humidity ~40% RH.
2. Reticle was stored in the commercial reticle pod in a cabinet purged with nitrogen. (Reticle pod was not purged.)
3. Reticle was stored in the purged reticle pod with discontinuous XCDA purge 3 slm. (Entegris RSP2 pod – purge, with no purifier.)
4. Two reticles (a, b) were stored in the purged reticle pod with continuous XCDA purge of 3 slm (Entegris RSP3 pod - purge with purifier [1].)

The results of these tests are presented in Table 3.

| Test # | Storage condition outside the scanner | Number of wafers printed before printable haze developed |
|---|---|---|
| 1 | No purge, 40 % RH | 2,500 |
| 2 | N2 cabinet, no purge in the pod | 11,000 |
| 3 | XCDA 3 l/min, discontinuous purge, RSP2 | 3,500 |
| 4a | XCDA 3 l/min, continuous purge, RSP3 | 55,470 |
| 4b | XCDA 3 l/min, continuous purge, RSP3 | 37,800 |

Table 3. Test results

## 5. CONCLUSIONS

The results of our tests well exceeded the lithographers' expectations. (See results for tests 4a and 4b in Table 3.) The two reticles protected by a continuous XCDA purge printed 55,770 and 37,800 wafers respectively, much more than the original target of 25,0000 wafers printed before the reticle required cleaning. Even more – these reticles retired without developing any haze related defects.

So, the 20 times improvement achieved in the experiment is the conservative estimate of the effectiveness of the XCDA purge as a solution to reticle haze. (Compare tests 1 and 4a in Table 3.)

The next step is to implement this solution on a full scale: Install a fully XCDA-purged reticle stocker and eliminate the need for individual reticle pod purge stations. This work is underway, and we intend to offer the results for presentation at the SPIE Microlithography 2008 Conference.

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# APPENDIX

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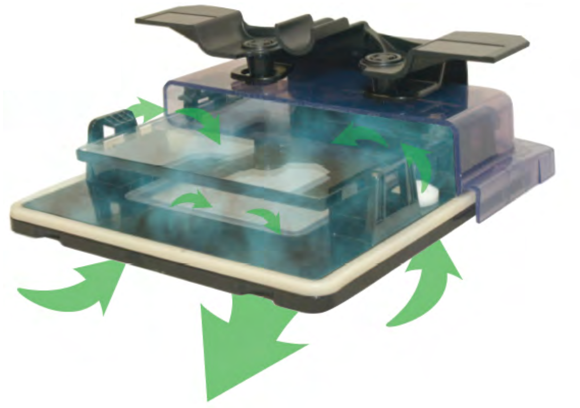
Picture 1. The RSPX Manual Purge Station is part of Entegris' Clarilite Certified solution for preventing reticle haze. The RSPX station gives manufacturers greater protection against reticle haze by purging the reticle pod as it waits for the next process step.



Picture 2. RSP3 reticle pod with purifier

The Entegris RSP3 reticle pod designed to protect reticles during transit and storage provides protection from Airborne Molecular Contamination. Picture 2 displays a cutaway view of the pod with a reticle and the purifier located on the center base of the pod.

The concept of the purifier is to act as a passive "sponge" for contaminates (acids, bases, and organics) that are in the pod or may enter the pod during transit, storage, and operation. These contaminates migrate their way into the pod and are the primary suspects causing reticle haze formation during UV exposure.