The Crystal Growth and Reticle Degradation Exposé

Reticule Surface Contaminants and Their Relationship to Sub-pellicle Particle Formation

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Crystal growth and haze formation on reticles continues to be a significant source of concern for the semiconductor industry. Possible sources, causes, and formation mechanisms continue to be investigated. Mask making materials, process residues, reticle containers and fab and or stepper environment can contribute to reticle degradation over time. This paper provides a comprehensive evaluation of various molecular contaminants found on the backside surface of a reticle used in high-volume production. Previously, all or most of the photo-induced contaminants were detected under the pellicle. This particular contamination is a white “haze” detected by pre-exposure inspection using KLA-Tencor TeraStar STARlight™ with Un-patterned Reticle Surface Analysis, (URSA). Chemical analysis was done using time-of-flight secondary ion mass spectroscopy (ToF-SIMS) and Raman spectroscopy.

Introduction

Sub-pellicle reticle contamination was first reported by Grenon et al.¹ as a major concern in high volume semiconductor fabs. Bhattacharyya et al.² identified some of the contaminants as cyanuric acid and ammonium sulfate. Since the initial report, many cases of particle or contamination formation on both 248 nm and 193 nm reticles have been reported. While reported cases of the problem have been increasing as 248 nm lithography becomes more ubiquitous, the introduction of 193 nm lithography in leading-edge fabs has resulted in reports of haze and contamination formation on reticles at greater numbers and at a faster rate.³

As lithographers move to shorter wavelengths, it can be assumed a priori that molecular contaminants in the path of light will be more reactive and possibly effect transmission more radically than at higher wavelengths. While reticle surface contamination has been identified as a significant issue at 157 nm, it is rapidly becoming a critical issue at 248 and 193 nm. It should be noted that the pelliclized reticle structure creates an almost perfect photochemical reaction chamber. Figure 1 shows the basic structure of a pelliclized production reticle.
The intra-pellicle space can trap molecular contaminants and provide an opportunity for them to react and deposit on reticle and pellicle surfaces. Note that the inner surfaces of the pellicle have several adhesives: a film adhesive that is often cyanoacrylate, the inner frame wall adhesive (IFW), and the frame adhesive. These materials out-gas and can potentially cause crystal formation in the optical path of the reticle. Additionally, surface contaminants on the metal mask and quartz surfaces can out-gas and be trapped in this space.

Because the reticle user identified this problem, this investigation focused on identifying the chemical composition and possible cause(s) of the backside quartz haze. However, it should be noted that identical haze was detected on the inner surface of the reticle storage box, as well as in the intra-pellicle surfaces.

**Defect detection and identification**

**Defect Inspection Method — TeraStar STARlight with URSA**

The reticle analyzed in this study was inspected using the above systems and software options, and was sent for chemical analysis. The URSA option first detected the haze on the backside quartz surface of the reticle. The advantages of this technique are that it provides inspection capability for both surfaces of the pellicle and for the backside surface of the reticle. URSA employs laser scattering illumination and detection technology to find particles, smudges, fingerprints and other handling defects on unpatterned reticle surfaces. STARlight and URSA combined inspection, provides the capability to inspect all the surfaces of a reticle (patterned surface, backside quartz, chromium, and inner and outer surfaces of the pellicle). The features of this inspection technique are:

1. URSA provides a sensitivity of 4 µm (on PSLS) in about two minutes/surface.
2. Darkfield defect preview on pellicles and glass while URSA or STARlight inspections are in progress.
3. Defect review order from largest to smallest.


5. User adjustable sizing box for defect measurement.


7. View reticle pattern under a defect on pellicle or glass.

These capabilities allowed detection of the contaminants on the reticle prior to any potentially catastrophic use of the reticle in production. Figure 2 provides a brief overview of the basic URSA defect detection system.

**Results of Defect Inspection**

A 6.0 x 6.0 x 0.25 inch pelliclized reticle was inspected on TeraStar STARlight with URSA following extensive exposure in the fab. The results of the inspection indicated a significant level of haze on the backside quartz surface of the reticle. Other defects were evident on the front side of the reticle under the pellicle. For the purposes of this investigation we focused on identifying the composition and magnitude of the haze contamination of the backside of the reticle. Figures 3 through 5 provide data generated during the reticle inspection.

**Defect Identification**

Following defect inspection, the reticle was submitted for chemical analysis. Both Raman spectroscopy and
ToF-SIMS analysis were done on several defective areas of the reticle. Figure 6 provides images of the locations of the analyses.

Raman spectroscopy was accomplished on two of the haze defects that were small amorphous defects in the range of 1.0 µm. These defects were representative of all of the other haze-type defects on the reticle. The Raman spectra were collected using a Renishaw Model Raman spectrometer equipped with a 633 nm laser. The beam size was approximately 1.0 µm in diameter. Background spectra were collected on the quartz surface in order to cancel out the possibility of contamination due to transport and handling during the analysis. The results show the haze to be one compound, ammonium sulfate. Figures 7 and 8 show the spectra for the defects analyzed. These spectra are consistent with the spectra previous reported for ammonium sulfate. The possible sources and mechanism of the formation of this contaminant will be discussed later.

In order to verify the elemental composition of the haze defects, we conducted ToF-SIMS analysis on the quartz surface of the backside of the reticle. The instrument used in this work was an ION-TOF, TOF-SIMS IV™ secondary ion mass spectrometer. In this technique, due to the low primary ion fluence, only outer surface monolayers are probed (i.e. a few angstroms). The actual damage to the sample is very low, and thus the method is ‘quasi non-destructive’ or static in nature. This technique provides not only elemental information about the surface, but chemical information as well, in the form of fragmentation patterns of molecular species.

A 15 kV, pulsed 69Ga+ primary ion beam was used for analysis, by impinging upon the sample surface and creating secondary ions in a process known as sputtering. The primary gallium beam was rastered over a 500x500 µm² area in positive secondary ion mode, and 300x300 µm² in negative secondary ion mode. Both positive and negative secondary ions were collected and mass separated via the time-of-flight (TOF) analyser. A traditional first order mass spectrum was then produced by plotting the ion intensity at a particular mass (more specifically, mass to charge ratio, m/e; however, the vast majority of species of interest are singly charged). The
mass range for this work was 0 - 1000 AMU with a maximum of 10,000 possible; however, acquisition time increases with increasing mass range. The nominal resolution approached 10,000 above 200 AMU. The technique has a detection limit approaching PPM levels, depending on the species of interest. As the secondary ion yields are matrix dependent, the technique is not quantitative on an absolute scale, although this may be overcome via the use of appropriate standards.

Figure 9 provides the results of the ToF-SIMS analysis. The intensity scale indicates the relative concentrations of the various ions detected on the surface. The brighter the ToF-SIMS image, the greater the relative concentration of that ion. The figure shows the ions of interest. It is important to note that other significant contaminants were found on the surface and are not shown here. The left side of the figure provides a ToF-SIMS image of the ammonium ions that compose the haze. The remaining images show both the positive ammonium ions and the sulfate ions on the surface.

It is clear from both the Raman spectroscopy and the ToF-SIMS analysis that the haze on the reticle is ammonium sulfate.

**DISCUSSION**

*Chemical Mechanism*

The most common method for reticle cleaning in the photomask industry is the use of sulfuric acid and hydrogen peroxide at elevated temperatures, often followed by a dilute ammonium hydroxide rinse. While the chemistries are similar from mask facility to mask facility, the process recipes can change significantly. The recipes can even vary within a mask facility. This is probably because not all reticles behave in the same manner when exposed. These chemistries can leave residues on all surfaces of the reticle if improperly rinsed; they also react with the quartz surfaces. Some of the more common reactions that can occur are the formation of silicic acid or hydrated silicon dioxide. The ammonium rinse can form ammonium silicate. Figure 10 provides the possible mechanism for the formation of the haze on this reticle. While this may be the most likely cause, it does not obviate other potential causes or mechanisms for haze formation on reticles.

While surface absorbed ammonium ions are the most probable source of the ammonium ions; other environmental sources of ammonium ions could cause the formation of the ammonium sulfate. However, in most fabs where chemically amplified resists are used, activated charcoal filters are used to filter out ammonia and ammonium ions; therefore, environmentally deposited...
ammonium ions are an unlikely source. Sulfate ions are not labile (likely to easily undergo chemical change), therefore it is mostly probable that these ions were on the reticle as a cleaning process residue. Other possible sources of sulfate ions could be environmental, however unlikely this is. Unpublished results have shown high concentrations of sulfate ions on all mask surfaces following mask cleaning.

**Exposure Conditions for Haze Formation**

While exposure conditions for particle and haze formation can vary significantly from fab to fab and from reticle to reticle, exposure conditions under which the haze formed on the reticles in this paper are well understood. Figure 11 provides data for several reticles that have shown haze formation on both the backside, as well as the chromium side of the reticles.

The above chart indicates that the formation of contamination defects is linear for 248 nm exposure and almost exponential with dose for 193 nm. For this reason reticles exposed at 193 nm provide a greater risk for catastrophic failure in the fab; hence, they should be inspected at a greater frequency.

**Conclusions**

Crystal growth and haze formation on reticles continues to be a significant source of concern for the semiconductor industry. Possible sources, causes and formation mechanisms continue to be investigated. Mask making materials, process residues, reticle containers and fab and or stepper environment can contribute to reticle degradation over time. In the case of this study, we feel that the most probable source of the haze formation was residues left on the reticle during the fabrication process.

Backside glass haze can effect overall mask transmission and thus can cause a dose shift on the wafer. A dose shift can be serious because most low k₁ processes run with a very small process window and therefore a small dose shift can create a serious yield issue. The backside haze can be easily and reliably detected by Starlight URSA inspection. An ideal quality control approach is to detect any possible reticle degradation prior to any catastrophic failure in the fab. This can be accomplished by re-inspecting reticles prior to exposure. It is recommended that a carefully-developed reticle inspection strategy be implemented to minimize mean-time to detect defect growth. This is best done by understanding the cumulative dose seen by the reticle and correlating it with the first detection of reticle degradation. These values will vary as a function of wavelength and exposure dose in the fab. As a result, each fab should develop specific inspection and re-qualification plans for reticle.

The rate of contamination formation on these reticles was significantly faster at 193 nm exposure than at 248 nm, hence a greater inspection or re-qualification frequency would be recommended for 193 nm lithography.

**Reference**


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"Remember that 'nuisance' reticle defect everyone ignored?"

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