Haze Risk Reduced Mask Manufacturing Process

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ABSTRACT
Since introduction of 193nm exposure wavelength, the haze formation becomes a serious challenge especially at masks used for big number of exposures. Several compounds present in air as low concentration contaminants are leading to haze building. Well understood is the sulphate based haze formation, however, still causing significant losses and demanding for re-cleaning of the mask during mask life time.

There are plenty of publications taking different approaches to reduction of the final sulphate concentration on the mask and reduction of the use of sulphuric acid during the mask manufacturing. Beside traditional process as hot water extraction, UV exposure, baking, IR exposure at vacuum, Ammonia solution treatment more exotic method were published as surface treatment preventing migration of the sulphate ions on mask surface. The number of exposures till haze crystals growth prevents further use of the mask is not solely dependent on the sulphate concentration on the freshly manufactured mask. Additional factors as storage and use conditions are significantly influencing the period till re-clean of the mask is needed.

In this work we try to assess above mentioned approaches and provide rough estimate of their limits.

INTRODUCTION
Ammonium Sulphate was recognized as major haze source for 193 nm exposure in late 90. There are several other materials causing haze growth as e.g. oxalates, but the broad usage of sulphuric acid for cleaning of photomasks combined with very low concentration of sulphate, air humidity and ammonia air contamination leading to haze formation are reason for the focus on sulphate haze.

As mentioned in many publications, the haze crystals are growing during mask usage and are mainly exposure induced. For successful reduction of the haze occurrence not only the mask manufacturing, but to same degree the mask handling and treatment during exposure and storage at wafer fab are important. Inappropriate storage of masks is comparable to post clean contamination of the mask during the manufacturing process and such issue can not be solved by change of mask manufacturing process, however, there are factors influencing the susceptibility of the mask to post clean contamination as we will show later on. One in literature mentioned approach is blocking of the sulphate molecules adsorbed on the mask surface by additional treatment of mask surface for HT-PSM mask.

The main task for clean processes with respect to haze remains the reduction of sulphate contamination of the mask, usually measured as concentration of sulphate in water sample, extracted at defined conditions and analyzed via ion chromatography (IC).

Main focus of our work is to estimate the effectiveness of sulphate removal by previously mentioned processes and provide rough estimate of the critical contamination level at the freshly manufactured mask.

The task for cleaning process with respect to sulphate is to remove the contaminant from surface and bulk of mask and protect the surface against future contamination after the cleaning process.

Following chemical reactions lead to creation of ammonium sulphate.

Ammonium chemisorption:\[ SiO_2 + H_2O_2 + H_2SO_4 \rightarrow Si(OH)_4 + NH_4OH \rightarrow SiO_4^{2-} (NH_4^+)_4 \]

Sulphate creation:\[ SO_2 \xrightarrow{\text{adsorption}} \rightarrow SO_2 \]

Oxidization of sulfur dioxide \[ O_2 \xrightarrow{\text{hv}} 2(O) \rightarrow O + SO_2 \rightarrow SO_3 \]

Formation of sulfuric acid \[ SO_3 + H_2O \rightarrow SO_4^{2-} + 2H^+ \]
Sulphate formation \[(NH_4)_2SiO_4^{-2} + 2(SO_4^{2-}) + 4(H^+) \longrightarrow 2(NH_4)_2SO_4 + Si(OH)_4\]

Last reaction is chemical reaction between adsorbed ions on mask surface.

There are several approaches in use for reduction of Sulphate level;
- Water extraction,
- Bake – sometimes combined with UV exposure and
- Vacuum treatment.

Some authors report methods for sealing of the mask surface to avoid diffusion of sulphate ions to the mask surface or blocking the adsorption center to avoid further contamination of the mask from environment. In these processes following physical and chemical mechanism are involved:
- Solid - Liquid extraction
  The extraction rate and equilibrium is dependent on surface area and diffusion path length, which can not be changed. Since sulphate molecules are polar, use of polar liquid as water is advantageous as well. For successful extraction also the solubility of sulphate in given liquid, surface energy solid-liquid between solvent used and the mask surface are important as well as the solvent viscosity\(^1\). The extraction rate is strongly influenced by diffusion of sulphate molecules towards surface and transport of extraction liquid through the bulk.
- Thermal desorption
  Desorption rate of sulfur dioxide and trioxide is driven by temperature according to following equation.
  \[ R = A \cdot e^{-\frac{E_a}{kT}} \cdot N^x \]  
  Where \(A\) is attempt frequency, \(E_a\) is activation energy of desorption, \(k\) is Boltzmann constant, \(T\) is temperature and \(N^x\) is concentration of adsorbent power to kinetic order of desorption.
- Heat decomposition
  Thermal decomposition of sulphate / sulfuric acid is thermodynamically possible at temperatures above 360°C\(^6\). Such high temperatures can not be used for baking of the mask without affecting strongly the registration. At temperature of about 220°C and above the influence of bake process is measurable as typical distortion of the mask blank as we will show later.
- Haze crystallization followed by dilution in water
  (NH\(_4\))\(_2\)SO\(_4\) haze crystals observed on exposed masks are known to be removable by soft clean process. The ammonia sulphate crystals have very high solubility in water of (754 g/l at 20°C, 843g/l at 50°C).\(^{10}\) Main contributor to removal mechanism of haze nuclei / crystals is dilution in water.

Following methods were proposed as alternatives reducing the haze crystal nucleation and growth by modification of surface
- Sealing of bulk contamination to avoid haze crystal growth during mask exposure
- Blocking of adsorption centers on surface

**METHODOLOGY**

Sulphate level at the end of each experiment was estimated as follows. Mask blank was extracted at 90°C by 100 ml DI water. Subsequently the water sample and reference sample were analyzed using IC. The analysis of the reference sample is used as check of used water purity to avoid systematic error by contamination of sample from different sources. The values estimated at identically prepared samples are significantly higher than numbers obtained at Chemtrace lab. To provide readers an idea of the relation between Chemtrace and AMTC results, correlation curve between both methods is shown in Fig.1.

For sulphate the detection limit of the analysis at given setup is about 0.1 ppb. The contamination of reference sample was in all cases below detection limit and the result obtained at water sample can be used as measured. Due to the experiment setup the concentration measured represents whole mask surface - front side, back side and the side wall. The surface of the front side and the back is 232.2 cm\(^2\) each; side wall surface is 38.71 cm\(^2\). We have to take into account that the areas of the front side and the back side of the mask represent about 46.2% each of the total surface; the side wall surface is about 7.6%. As we will show later, the contribution of the back side to the total sulphate level is almost negligible, due to the fact, that quartz surface is adsorbing sulphate to very low level as we will show later.
Sulphate removal effectiveness was measured using Hoya AR8 COG mask blanks contaminated to high level by sulphuric acid wet process and rinsed subsequently by cold water in order to get representative and well reproducible results.

**Fig. 1** – Correlation between analysis results obtained from AMTC analysis and Chemtrace analysis. Chemtrace analysis is in contrary to the AMTC procedure performed on the front side of the mask only. Further difference is lower temperature of the extraction water at Chemtrace method.

The sulphate removal effectiveness is strongly dependent on the surface material. Due to the varying density of adsorption centers and different surface area the concentration of $\text{SO}_4^{2-}$ differs when comparing chrome, chromium oxide (ARC), MoSi A61A and quartz surfaces.

Among COG mask blanks Hoya AR8 COG Mask blank is to our knowledge the most sensitive production material used nowadays for high end mask manufacturing due to the thick absorber and especially the CrO$_x$ ARC layer acting as buffer for sulphate. Reduction of the ARC layer thickness leads to strongly reduced concentration of adsorbed sulphate. Further strong decrease is observed when Chrome absorber without ARC layer is analyzed followed by oxide and nitride materials Hoya A61A MoSi layer, ShinEtsu binary absorber (OMOG) without hard mask and quartz substrate.

**Fig. 2** shows comparison of the susceptibility of materials mentioned in text. At first look one can see significantly higher sulphate level at Chrome materials AR8, NTAR5, NTAR7, TF11 decreasing in listed order from 200 ppb down to 95 ppb. Non metallic materials as A61A MoSi, OMOG without hard mask and Quartz show significantly lower level below 10 ppb. The effect of ARC layer at chrome surface can be judged by comparing sulphate level of NTAR5 to CR material, having comparable Chrome layer thickness as NTAR5 chrome layer, but no CrO$_x$ ARC layer.

**Fig. 2** – Sulphate concentration estimated at different materials after sulphuric acid and cold water treatment. Chrome surfaces exhibit significantly higher sulphate level then MoSi, OMOG absorber and quartz surfaces. Tested materials are Chrome - AR8, NTAR7, NTAR5, TF11, CR, MoSi - A61A; OMOG without hard mask and Quartz. White rectangles at the top of each bar represent the uncertainty of the estimation caused by blank to blank variation, contamination process and analysis reproducibility.
WATER EXTRACTION

The easiest method used for sulphate level reduction is water extraction. Since both cold and hot water are available at any clean tool, there is no need for hardware modification and the process setup is rather simple as well. The process can be described as solid-liquid extraction with known parameters influencing the thermodynamics and kinetics of the process.

The $\text{SO}_4^{2-}$ extraction rate from mask surface is driven by water temperature and so the final $\text{SO}_4^{2-}$ level is dependent on the process time and temperature only. Further factors as e.g. media flow, nozzle-mask surface distance or arm movement were not significant with respect to $\text{SO}_4^{2-}$ concentration. The effect of temperature is very strong. For sulphate removal rate higher water temperature is of advantage, however, hot water temperature is limited by several factors:

- hardware limitation – water heater power and heater control characteristics
- raising level of defect originating from material extracted from heater / tubing between heater and nozzle
- phase change of a half tone phase shift mask (HT-PSM) is raising with increasing water temperature, especially if chemistry doped hot water is used

For above listed reasons the temperature has to be chosen, at which the hot water defects are within acceptable limits, the tool heater lifetime is not impacted (vapor bubbles generation) and the phase change per clean is within specification.

Fig. 3 – Effect of rinse water temperature estimated on AR8 mask blanks at constant media flow of about 2 l/minute and extraction time of 20 minutes. Water temperature was varied between 20 and 83 °C.

Second parameter, one has to optimize, is rinse time. The impact of rinse time on $\text{SO}_4^{2-}$ concentration is nonlinear as one can see in Fig. 4. In the beginning of the process the sulphate concentration reduction is very fast and decreases with increasing rinse time significantly. At given temperature the process stops at certain nonzero sulphate concentration. At tested conditions the $\text{SO}_4^{2-}$ concentration reaches level of about 13-15 ppb after about 2000s rinse time and is not changing anymore with increasing rinse time. The logarithmic plot of the $\text{SO}_4^{2-}$ concentration (Fig. 4) identifies change in the kinetic of the $\text{SO}_4^{2-}$ extraction. The first part of the process from beginning to approx. 1000s represents in our opinion desorption from mask surface. In the second part, the kinetics is assumed to be driven by diffusion of the $\text{SO}_4^{2-}$ molecules from ARC layer bulk material or transportation through material grain boundaries to the surface, followed by desorption from the surface, which is the faster process and increases the driving force of the diffusion.
**Fig. 4** – SO$_4^{2-}$ level as function of rinse time. The temperature of hot water used is 83°C measured at impact point; water flow is 2l/minute. SO$_4^{2-}$ extraction was measured at Hoya AR8 mask blanks pretreated by sulphuric acid and cold water rinse to SO$_4^{2-}$ level of 200±7ppb; Logarithmic plot of SO$_4^{2-}$ concentration as function of hot water rinse time is nonlinear as one can expect for extraction process. The SO$_4^{2-}$ extraction is driven by different processes at different rinse time. This fact leads to decrease of desorption rate and limits the hot water extraction at given temperature to final level of about 13-15 ppb. Whereas at the rate at the beginning of the process is limited by desorption from surface (grey area), later on the dominant process is transport of ions from bulk material via diffusion (white area). At rinse time of about 2000s the base level is reached and further rinse does not reduce the SO$_4^{2-}$ level as measured via IC.

As mentioned previously the limitation of the hot water rinse are phase angle change and defect level – limiting both temperature and process time. Figure 5 shows influence of hot water rinse on mean phase change at 83°C hot water process. Phase change measured using hot water rinse only seems to be very small, however, combined with remaining clean process, the hot water rinse contribution significantly increases. Similar, the phase change measured using clean process without hot water rinse is significantly smaller than using full clean process (see Fig.5). Since the phase change for full clean process is not equal to phase change of its component, the effect can be explained by interaction between hot water rinse and remaining process steps only. Which steps interferes with hot water rinse is not known yet. Mixing of the hot water with ammonia, ozone and many other frequently used chemicals leads to significant raise of the phase change compared to shown level as observed by many authors e.g.11.

**Fig.5** - Phase angle change as function of hot water rinse time using CO$_2$ doped water heated to 83°C. Phase change measured using hot water rinse is very small (solid line). Phase change estimated is -0.137 °/hour using 83°C hot water doped with CO$_2$. Combining this rinse step with ready to use particle removal clean process leads to significant phase change increase of -0.21 °/hour (dashed line). This discrepancy in phase change indicates strong interaction between steps in clean process.

**UV EXPOSURE/HOT PLATE BAKING**

The UV treatment and bake used separately have relatively low efficiency. Both processes support desorption, UV exposure decomposes sulphate as well as bake at very high temperatures. UV exposure is reported to force transfer of ions in direction of exposure - towards mask surface when exposed on the back side and towards mask bulk when exposed on the front side5. 3 minutes UV exposure at 172nm wavelength in dry air reduces sulphate concentration from 200ppb down to approx. 140ppb. Further increase of exposure time does not reduce the sulphate level significantly. Baking of the mask at 200°C for 10 minutes leads to decrease of SO$_4^{2-}$ level to about 90 ppb. SO$_4^{2-}$ molecules decompose at very high temperatures of about 350-400°C 6,10. Such high temperatures are not applicable for mask cleaning process. That is, the reason for assumption, that the mechanism of this SO$_4^{2-}$ concentration reduction in this case is desorption. Best results were obtained by combination of UV and bake steps followed by water rinse. There are strong interactions between factors between involved process steps. In Figure 6 interaction between UV exposure time and bake temperature is demonstrated. High environmental humidity increases the nucleation and growth of haze crystals. Reasons for the humidity effect are reactions leading to transfer of sulfur oxides to sulphate, where water is involved and transfer chemisorptions of ammonium ions on silica surface 9. The mechanism of the nucleation and crystal growth is discussed in detailed by Wu at al 2.
In general, as expected, high temperatures are advantageous for sulphate reduction. There are several more interaction between parameters as e.g. gas composition and UV exposure which we do not discuss in detail.

As mentioned previously disadvantage of very high temperature at bake step is distortion of the mask, measurable as registration. In order to avoid such distortion, the bake step has to be extremely short, what impacts negatively the sulphate removal process, or alternatively the maximum bake temperature has to be limited to 250°C. The distortion of the mask originates from very small decrease of the viscosity of amorphous quartz substrate heated up. Even thought the glass transition temperature for quartz is about 1200 °C, the effect of distortion is measurable already at 220°C, which is less than 20% of the glass transition temperature. Figure 7a shows the permanent registration change measured at 193 nm HT PSM masks heated for 1200s to 250°C.

**VACUUM TREATMENT**

Treatment of manufactured masks before pellicle mounting by IR radiation in vacuum was proposed as effective sulphate reduction method. During this process the masks get heated up to about 150°C which is acceptable for all types of masks, even for EUV mask. The vacuum treatment is reducing the sulphate level without any side effect on defect level. Impact of the relatively long process on CD, registration, Phase/ Trans was not reported. This process in our opinion is the most gentle one with respect to the mask properties. Disadvantage of the process may be relatively long process time.
Short vacuum treatment (<1 hour) of a mask at pressure <0.1mbar in N₂ gas atmosphere at temperature of less than 60°C does not lead to significant reduction of the sulphate level. Within 2h treatment the sulphate level decreases from starting value of 200ppb down to approx. 160ppb. Further decrease of sulphate level is, similar to hot water extraction, very slow and has most probably same reasons. Transport of the sulphate/sulfur containing molecules from the absorber on phase shifter bulk material is diffusion process which is significantly slower than the solid-liquid extraction from the surface. More promising results can be expected at raised temperature, however, for such process identical limitations are valid as for bake.

**INFLUENCE OF EXPOSURE**

Illumination of the mask during exposure by 193nm UV light is enabling many photochemical reactions leading to contamination of the mask. Dissociation of molecular oxygen from air during illumination by shorter wavelength than 246nm is mentioned in literature as key factor leading to sulfur trioxide formation. Due to adsorption on the mask surface the concentration of reactants for ammonia sulphate is significantly raised compared to gas reaction. Formation of haze crystals reduces the portion of occupied adsorption sites at mask surface and leads in that way to propagation of the haze reactants concentration. Limitation of this haze source is the environmental contamination of the mask storage. The illumination drives also diffusion of ion contaminants through the bulk towards mask surface.

The contamination level of the absorber is influencing the timeframe until haze can be detected. This contamination originates from mask blank, processes used during mask manufacturing or environment during exposure and storage of the mask. Differences in lifetime of the mask depend on the absorber material used. Potential mask manufacturing processes which proved to directly impact Sulphate/haze level on the mask might be (but not limited to): embedding of sulfur, carbon or nitrogen from resist into absorber of the mask during etch. The environmental conditions play a crucial role in the dynamics of haze formation too. Humidity, airborne ammonia and sulphates would be only a few ingredients to mention.

Even for masks processed by identical clean processes and having comparable sulphate level measured by extraction at mask house, strong differences in maximum exposure count are reported by wafer fabs. This confirms the fact, that only portion of the haze sources can be identified by IC analysis. There is some maximum sulphate level above which the mask will exhibit haze formation after short exposure time. Further reduction of the sulphate level measured by IC does not necessarily leads to improvement of the mask life time, since the bulk contamination, one can not estimate via IC, becomes dominant. Figure 8 illustrates the expected relation between the sulphate level measured via IC and the maximum exposure count before haze formation. Below certain sulphate level threshold A, high exposure count B can be reached before haze crystals form on the mask. At low sulphate level the environment is permanent source of continuous contamination. In such case the environmental contamination or ions transported to mask surface from the bulk by UV radiation are limiting factors for haze formation. At sulphate level above A the starting mask contamination is limiting. In this case the sulphate concentration is high enough and air humidity and exposure lead to haze nucleation and crystal growth. This is the reason for low exposure dose till haze appears. Further increase of sulphate starting level does not change the dose to haze formation significantly, since only the nucleation and crystal growth is faster.

The maximum exposure dose to haze formation at low sulphate level depends not only on the environmental contamination, but on the mask material –its susceptibility to sulphate sorption and bulk contamination.

![Fig.8 – Expected probability of haze crystal formation. X axis represents sulphate level on the mask as estimated by IC analysis at the mask manufacturing time. Y axis represents exposure dose or number of wafers exposed. The color in diagram represents the](image)
CONCLUSIONS

For reduction of sulphate level within mask manufacturing several processes are available, having different advantages. None of the processes available today can be used alone for reduction of sulphate level after sulfuric acid process (about 200ppb) down to level acceptable for high volume manufacturing, which is about 20 ppb or less according to analytical protocol shown.

With respect to sulphate level, there is minor advantage for masks manufactured using thin Chrome layer as NTAR7. Cr layer without CrO, ARC layer or HT-PSM masks with high MoSi area. These materials exhibit strongly reduced affinity to sulphate sorption due to thinner ARC layer or absence of Chrome absorber respectively.

Using optimized process steps for all available techniques described above we can reach sulphate level below detection limit of 0.1 ppb using all sulphate free processes and less then 3 ppb sulphate contamination using sulfuric acid strip process followed by sulphate free clean processes (see Figure 9).

![Fig.9 – final sulphate level estimated on AR8, NTAR7, A61A, OMOG materials using: sulfuric acid strip process followed by sulfuric acid free cleans (left viewgraph); sulfuric acid free strip and clean processes (right viewgraph). Sulphate level measured using the AMTC protocol described above is below 3 ppb for all materials. Using sulphate free strip and clean processes, the sulphate level is below 0.5 ppb](image)

Very promising candidate for reduction of sulphate level is the vacuum treatment process, which needs to be investigated more in detail. The only so far known disadvantage of the vacuum process is very long process time compared to alternative processes.

According to our experience the sulphate level of less then 20 ppb is acceptable for mass exposure and is not causing any troubles unless combined with additional contamination from e.g. pellicle out gassing, storage environment, transport boxes etc.

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REFERENCES


