Investigation of Sulfate Free Clean Processes for Next Generation Lithography

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1 ABSTRACT

Today, haze and crystal growth on the reticle surface are still a primary concern of the microlithography industry. The crystals limit the reticle usage as they result in printable defects on the wafers. Numerous studies have been presented so far. The general belief is that different root causes can lead to crystal growth and haze formation, among them the contaminants on the mask surface from the clean processes.
In this paper we are investigating the potential of sulfate free clean processes based on ozonated and hydrogen water for the next generation of photomasks. Key parameters such as cleaning efficiency, as well as the impact of the chemistry on the mask optical properties will be presented. The potential of the chemistry will be discussed and compared to the standard cleaning processes.

Keywords: wet cleaning, NGL, photomask, contamination, ozonated water, hydrogen water, sulfate

2 INTRODUCTION

The cleaning process remains a critical step in the photomask manufacturing process because of the mask material susceptibility to the chemistry applied. Throughout the years, the clean processes were all wet based on sulfuric acid-peroxide mixtures, known as SPM in combination with ammonia –peroxide mixtures also called APM or SC1.

The SPM provides strong oxidation capability to primarily deal with the organics on the mask surface. The SC1 on the other hand deals with inorganic particles and is every efficient in combination with Megasonics. The major drawback of SC1 or alkaline solutions is their ability to remove the absorber film (MoSiON) of phase shift masks (PSM) resulting in significant phase loss, and thereby limiting the number of cleans. Furthermore, throughout the last couple years, these chemistries were shown to actively participate to haze and crystal formation on the mask surface. This issue is significantly affecting the industry. Indeed, crystal growth results in printed defects on the wafers. Numerous studied showed that the residuals from these chemistries on the mask surface are contributors to crystal growth [1,2] on the same. The need for alternative cleans is strong and it becomes a necessity to investigate sulfate free cleans.

Our approach is to look at different alternative chemistries, namely ozone water and hydrogen water. The concept of hydrogen and ozone water is not new to the semiconductor industry and electrolyzed water has shown excellent ability to clean the surfaces of silicon and LCD substrates [3]. However the application to the mask clean process remains an ongoing development [4,5].

With an electrochemical potential of 2,08V, ozone is one of the strongest oxidants available. This suggests a good cleaning efficiency for organic contamination without the drawback of leaving ionic residues and makes the ozone a promising candidate for replacement of SPM. Moreover ozone is a green chemical, it can be produced when it’s required at the point of use solely out of oxygen gas. After the process the remaining ozone quickly decomposes back to oxygen gas, leaving no gaseous or aqueous waste that requires costly treatment nor pollutes the environment.

Hydrogen water on the other hand is reported to have the capability to neutralize the electrostatic adhesion forces of inorganic particles on photomask surfaces [4]. In combination with megasonics an effective removal of inorganic particles shall be possible. Because only small amounts of ammonium hydroxide are added to the hydrogen water to adjust the pH value, contrary to SC1 only low impact on MoSiON layers is expected, proposing the hydrogen water as a suitable alternative for SC1. Additionally, similar to ozonated water, hydrogen water can be produced at the point of use when required without the necessity of chemical supply from facility. It leaves no waste except DIW and small amounts of hydrogen gas.

In this work, we present the MaskTrack platform as the cleaning tool for photomask equipped with hydrogen and ozone water capability. Furthermore, we will present and discuss the results of the investigation of

the process parameters on the mask key optical properties, phase and transmission, reflectivity. Particle removal efficiency and cleaning efficiency will be reported as well.

3 MASKTRACK: TOOL CONCEPT

In order to meet the requirements for next generation lithography, STEAG HamaTech has developed a new tool platform for mask processing, the MaskTrack. The modular concept of the platform offers the flexibility to combine different modules to specific configurations. Extensions or upgrades of existing tools with new modules are possible without the necessity of replacing the tool as a whole. Fig. 1 shows the Masktrack cleaner installed at the AMTC for this study. Besides standard cleaning technology, such as SPM and SC1 it comprises ozonated water as well as hydrogenated water dispense systems through megasonics.

Fig. 1: Masktrack Cleaner at AMTC

Fig. 2a shows an insight into the process chamber of the cleaner. The dispense arms are parked in pans outside the chamber and covered with shutters during idle. They can be rinsed and dried in that position to remove particles and droplets from the outside. The chamber is aerodynamically shaped without edges and dead corners to ensure a laminar airflow through the chamber and to prevent turbulences and backsplashes during processes.

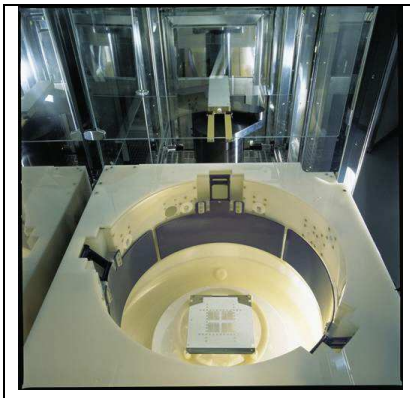

Fig. 2a View of Masktrack process chamber

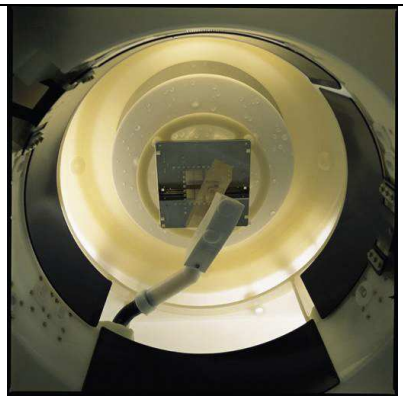

Fig. 2b Megasonic arm in process chamber

The tool is equipped with a 1MHZ and 3MHZ dual megasonics head (Fig. 2b) for dispense of ozonated water, hydrogen water and SC1, a jetspray arm for DIW rinse and a puddle nozzle for SPM dispense. The front- and backside of the substrate as well as the chamber can be rinsed with cold and hot CO2-ionised DIW.

4 PROCESS PARAMETERS INVESTIGATION

In order to evaluate the potential of ozonated water (DIO3) and hydrogen water (DIH2) and to find the optimum conditions for the new chemistry the performance of the media under different conditions was compared to the standard chemistry with respect to efficiency, substrate damage and residues.
For all experiments the acid ratio (H2SO4:H2O2) of SPM was 3:1, the SC1 concentration (percentage of SC1 in DIW) was 3% and the pH value of the hydrogen water was adjusted to 10.5 with ammonium hydroxide. The DIO3, DIH2 and SC1 was dispensed through a 1MHZ and 3MHZ dual megasonics nozzle. The temperature of hot DIW was set at 80°C.

4.1 Particle removal efficiency

The inorganic particle removal efficiency (PRE) of DIO3 as well as DIH2 was investigated and compared to SC1, which sets the standard in PRE today.
To carry out the experiments, chrome blanks were contaminated with calibrated Si_3N_4 particles with sizes in the range from 80nm to 2µm in a defined distribution. The blanks were then treated with the respective media, dispensed through megasonics. They were inspected pre and post to the clean on a Siemens DF 100-XP laser surface scanner with 80nm sensitivity.

In a first series of experiments the concentration of ozone in DIW has been varied in the range of 5 to 50ppm to investigate the influence of concentration on PRE. Fig. 3 shows the PRE as a function of DIO3 concentration. It can be seen that there is no significant connection between concentration and PRE. This result is consistent with other studies with megasonics where it was found that the major driver for particle removal is the presence of gas in the medium to enable cavitation. There is no strong dependence of PRE on concentration of the gas as long as it exceeds a certain threshold [6].
A similar series of experiments was performed to identify the optimum conditions for DIH2. The concentration of dissolved hydrogen was varied from 1,5 to 3ppm. As for the DIO3 no strong effect of concentration on PRE could be found.

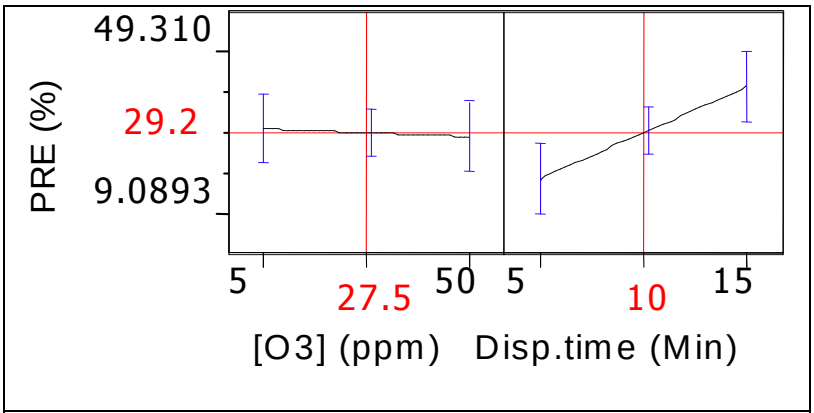

Fig. 3: PRE as a function of ozone concentration and dispense time

Comparison of the PRE of DIO3, DIH2 and SC1 under optimized conditions (Fig. 4) shows that SC1 has the best efficiency however DIH2 shows a remarkable efficiency as well. The PRE of DIO3 is low. This performance was reported before [4,7] and is probably because unlike SC1 and DIH2, DIO3 cannot neutralize the electrostatic forces between particles and surface that hinder the removal and promote the re-adhesion of inorganic particles.
Although, the PRE of DIO3 is poor in comparison to SC1 or DIH2, it does show much better removal performance than SPM. Taking into account that DIO3 is considered as the replacement of SPM for organic removals, it presents in addition significant removal capability for inorganic particles.

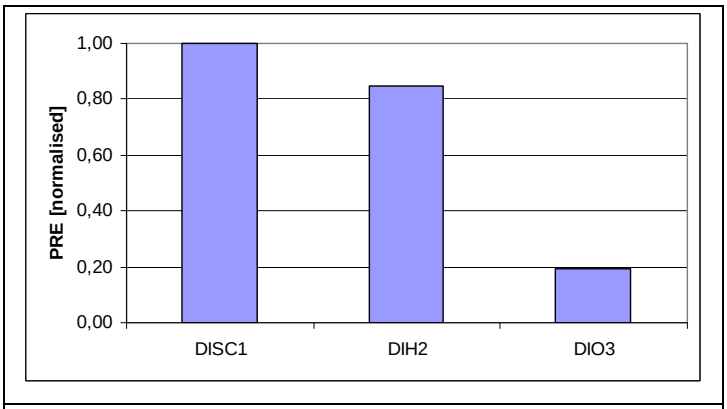

Fig. 4: Normalized PRE of DISC1 vs. DIH2 and DIO3

4.2 Cleaning Efficiency

The organics cleaning efficiency of DIO3 as a function of concentration and time has been investigated and compared to a standard SPM cleaning step.
Resist coated blanks were used for these tests in order to provide a typical non-particulate organic contamination that requires decomposition by the chemistry for removal. The remaining counts after the strip were measured on a Siemens DF 100-XP laser surface scanner with a sensitivity down to 80nm particles size.
Fig. 5a shows the remaining counts as a function of concentration after a 15min treatment with DIO3 at ambient temperature. The concentration was varied from 5 to 50ppm. It can be seen that the efficiency increases with higher concentrations. At the lowest concentration of 5ppm, the resist layer was still complete after the treatment.
The increase of the dispense time at a given concentration (27,5ppm) delivered the expected result, a decrease of the detections (Fig. 5b). The comparison of the DIO3 performance with a standard SPM treatment on Fig. 6 reveals that at a higher concentration, the DIO3 is actually slightly more efficient than the SPM. The data presented in those figures were obtained using NEB resist. A similar behavior was observed with FEP resist.

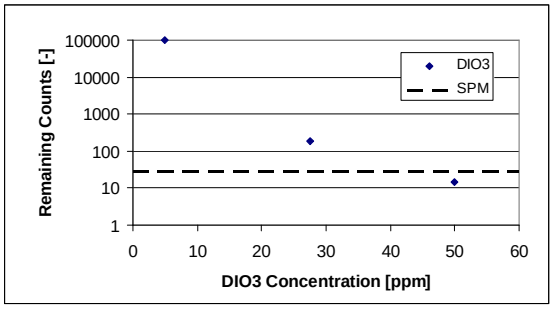

Fig. 5a: Remaining counts after strip as a function of ozone concentration vs. SPM

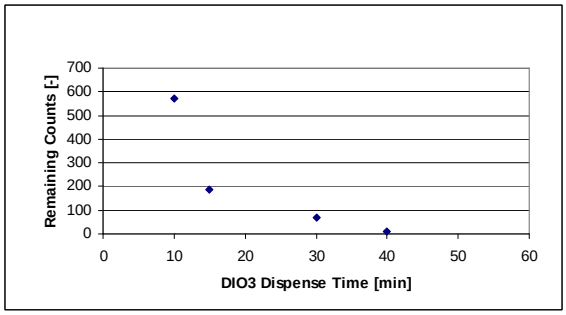

Fig. 5b: Remaining counts after strip as a function of DIO3 dispense time

In another set of experiments the capability of DIO3 to clean organic particles was compared to SPM. Chrome blanks were contaminated with PSL particles with a nominal size of 100nm to a level of ≈ 40000 counts. The plates were scanned, before, after contamination and after cleans, on the DF 100-XP from Siemens. The first plate was cleaned for 5min with SPM, followed by a 5min DIH2 step. The second plate was cleaned for 5min with DIO3, followed by a 5min DIH2 step. Fig 6 shows the result of these tests. It can be seen that SPM as well as DIO3 cleaned off all the PSL particles during that relatively short dispense. However after the DIO3 clean the count was even lower than before the contamination, i.e. the DIO3 did not only remove all PSL particles but even some of the baseline contamination.

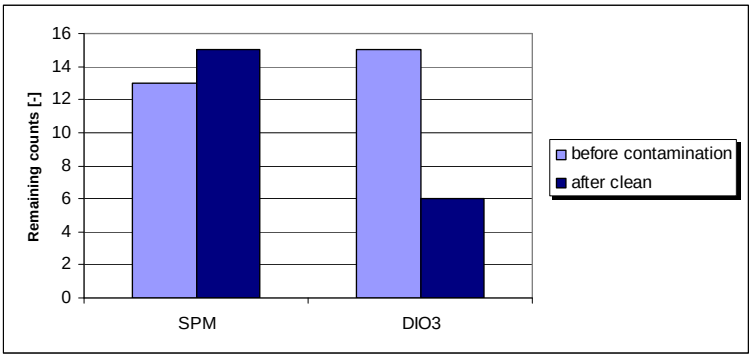

Fig. 6: PSL cleaning efficiency of SPM vs. DIO3

4.3 Phase and Transmission

Another important parameter to consider is phase and transmission change of MoSiON layers on PSM substrates. The application of hot DIW and SC1 for advanced photomask clean is limited by their strong influence on this parameter. In order to overcome these limitations, it is desired that new chemistries have a significantly lower impact. In this experiment the phase loss and transmission change of a DIO3 and DIH2 dispense was compared to a treatment with hot DIW and SC1.
Phase and Transmission was measured on a Lasertec MPM 193 tool on 9 locations across the plate.
Fig. 7a plots the average phase loss of hot DIW and SC1 versus DIO3 and DIH2 after an hour dispense. The dispense time was purposely exaggerated to clearly identify the impact of the fluids on the phase and transmission of the reticle. It can be seen that DIO3 and DIH2 have only a minor impact especially when compared to the significant phase movement from the hot DI water. Surprisingly, the SC1 showed a very low impact as well. A remarkable observation is shown on Fig 7b. After a treatment of the mask with DIO3, the properties of the MoSiON layer is virtually unchanged by a following dispense of DIH2 or SC1. Apparently the DIO3 not only has low impact on phase itself but moreover has the ability to passivate the MoSiON surface. Passivation of MoSiON layers was already reported [8,9] in connection with the usage of UV lamps. The authors found that actually oxidation of the surface through reactive oxygen is responsible for that effect.

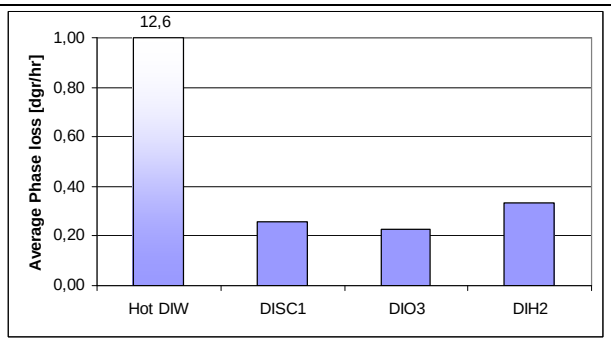

Fig. 7a: MoSiON phase loss after 1hr dispense of hot DIW vs. DISC1, DIO3 and DIH2

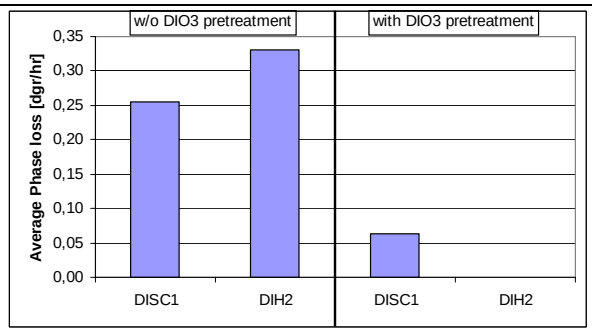

Fig. 7b: MoSiON phase loss after 1hr dispense of DISC1 and DIH2, with and without previous DIO3 dispense

The measured values for transmission change (Tab. 1) correspond to the findings from phase measurement. An increase in transmission is coherent with a decrease in phase.

Media		Transmission change [% Transmission]
Hot DIW		1,035
DIO3		0,008
DISC1		0,029
DIH2		0,027
DIO3 Pretreat	DISC1	0,015
	DIH2	0,001

Tab. 1: Transmission change of MoSiON substrates after 1hr dispense

4.4 Reflectivity

To investigate possible damage of the chrome AR layer by DIO3, the reflectivity change at 193nm of fresh Hoya NTAR7 chrome blanks was measured as a function of concentration and dispense time and compared to a standard SPM cleaning step. The reflectivity measurements were performed on the STEAG HamaTech AUV tool at 20 locations across the plate. Fig. 8a plots the average reflectivity change as a function of DIO3 concentration for a 15min dispense. The dotted line marks the reflectivity change for a 15min SPM treatment. One can see that for all measured concentrations the change is relatively small, 0,40% maximum and in the range of the SPM. For longer dispense times (Fig. 8b) the reflectivity change increases moderately. These results suggest that no damage to the chrome layer by the DIO3 for normal process times needs to be expected that is significantly more severe than from standard SPM clean.

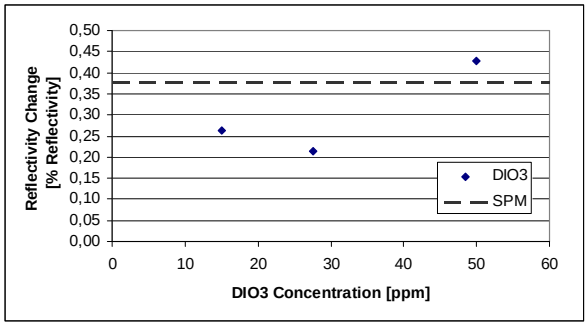

Fig. 8a: Reflectivity change at 193nm of chrome layer after 15min dispense as a function of ozone concentration vs. SPM

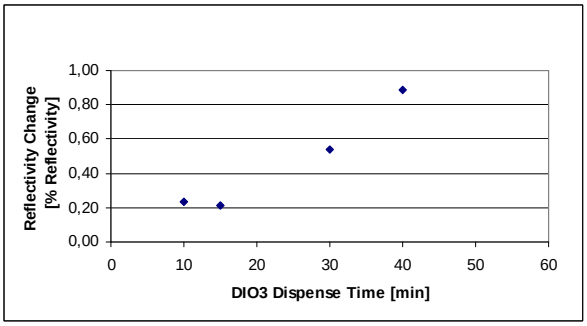

Fig. 8b: Reflectivity change at 193nm of chrome layer as a function of DIO3 dispense time

4.5 Ion residuals

Finally the capability of DIO3 and DIH2 to remove ion residuals, namely sulfates and ammonium was tested and benchmarked with hot DIW which is the common agent for residual removal today. For the experiment new resist coated blanks were stripped with SPM to obtain high residual levels and then treated with the respective media for a defined time. The residual level before and after the treatment was measured through hot water extraction and GC-MS analysis of the extract. The results are shown in Fig. 9. It can be seen that still the hot DIW has the best removal efficiency. For the DIO3 a dependency of concentration can be seen. The efficiency increases with the concentration and at 50ppm the DIO3 can reduce residuals at a considerable level. DIO3 with low concentration as well as DIH2 did only remove small quantities of ion residues.

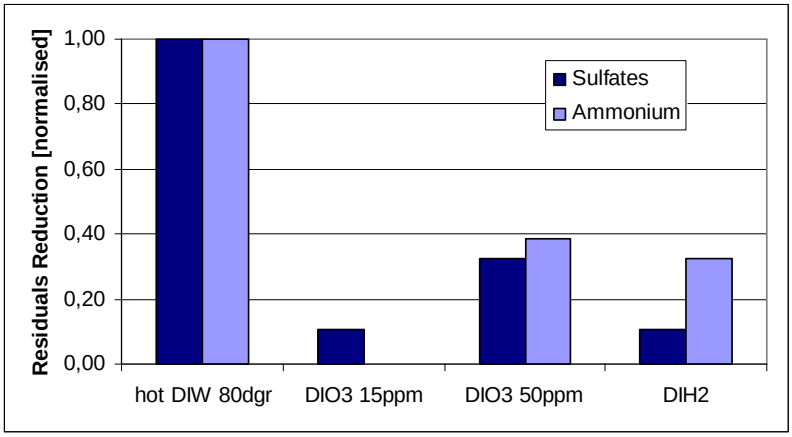

Fig. 9: Normalized ion residuals removed after 15min dispense of hot DIW vs. DIO3 and DIH2

5 PROCESS RESULTS

Based on the findings from above process recipes with the new chemistry were set up for resist strip and final clean. The performance was compared to the process of record with UV-treatment, SPM clean and SC1 clean through jetspray and megasonics.

5.1 Resist Strip

Figure 10 shows the normalized counts after the SPM SC1 process and DIO3/H2 process. It can be seen that DIO3/H2 process shows superior performance, approximately 40%. These results are very encouraging and are worth further investigation.

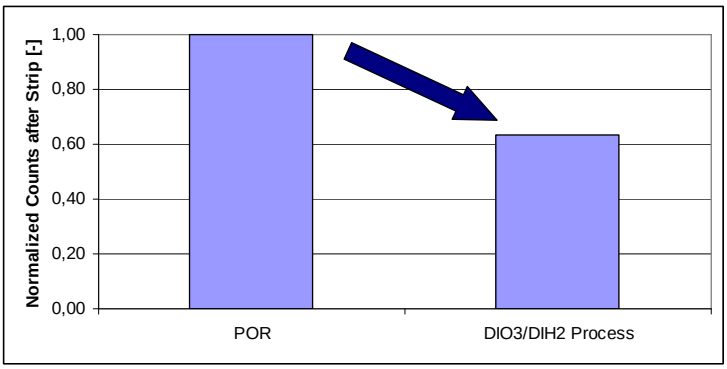

Fig. 10: Normalized strip residuals after POR and DIO3/H2 process

5.2 Final Clean

From the previous results, a final clean process was assembled, and tested on a high-end mask. Starlight inspection at 125 pixel size was performed before and after final clean. The results are summarized on Figure 11.

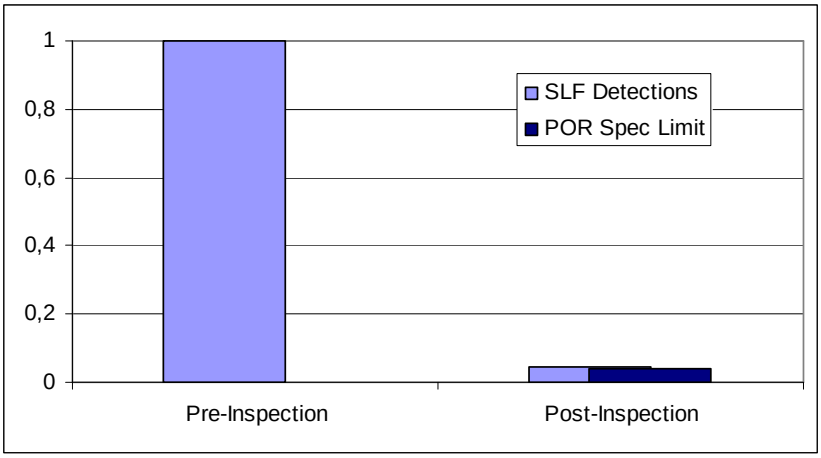

Fig. 11: Cleaning efficiency summary of Startlight Inspection of a high-end reticle.

96% cleaning efficiency was achieved. This result confirmed the good cleaning efficiency already observed on the blanks material with such chemistry. In addition, no structure damage nor AR damage was identified from the post-clean inspection.

6 CONCLUSION

In this paper we could confirm the feasibility of DIO3 and DIH2 for advanced photomask clean. With the new chemistry it was possible to achieve a cleaning performance that is at least comparable to the performance of standard cleans with SPM and SC1 without the drawback of leaving sulfate residues. The new chemistry did not damage chrome surfaces more severe than a standard clean and had only very low impact on phase and transmission of halftone PSM MoSiON layers.
The study could reveal some remarkable properties of DIO3. It can passivate MoSiON layers in a way that the impact of following clean steps on phase and transmission is significantly reduced and it can considerably remove sulfate residues. Out of these findings various possibilities for combinations and further optimisations of process steps arise with the potential to derive cleaning processes with high efficiency, low residual levels and low impact on pattern. This is the subject of further investigations.

ACKNOWLEDGEMENT

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