EXTENDING THE RUTHENIUM CAPPING LAYER LIFE TIME OF EXTREME ULTRA-VIOLET LITHOGRAPHY PHOTOMASKS IN PHYSICAL FORCE CLEANING

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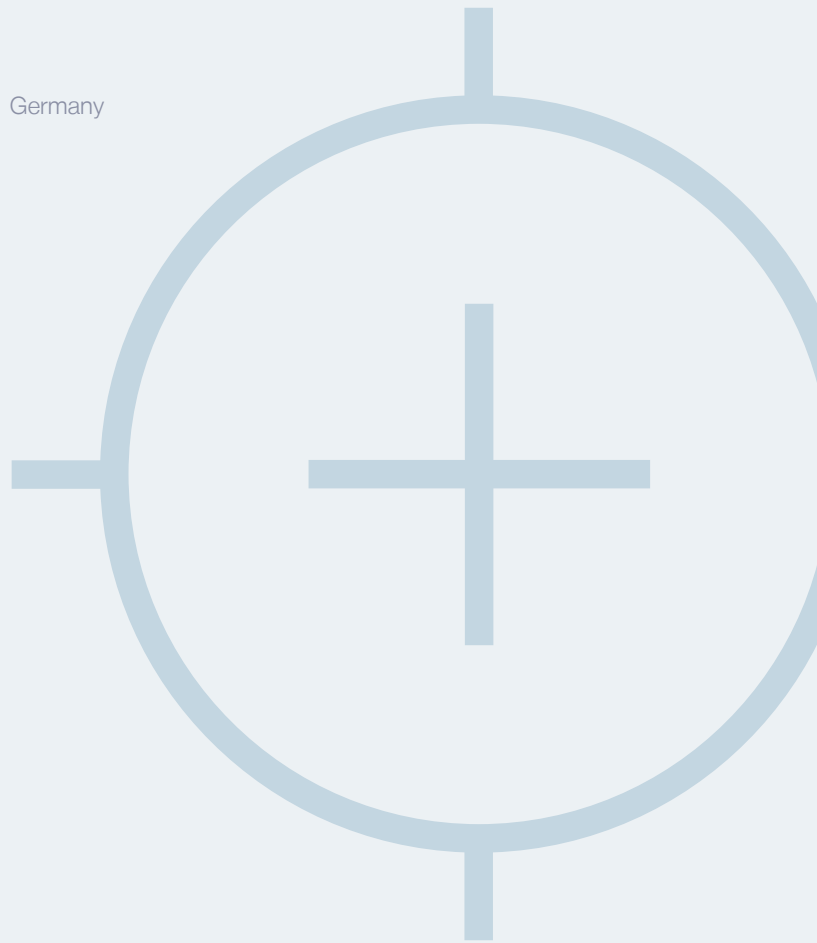
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1. INTRODUCTION

Extreme Ultra-Violet Lithography (EUVL) is currently considered one of the most promising Next Generation Lithography (NGL) choices to extend shrinkage of transistor sizes. This is also reflected in the International Technology Roadmap for Semiconductors (ITRS).
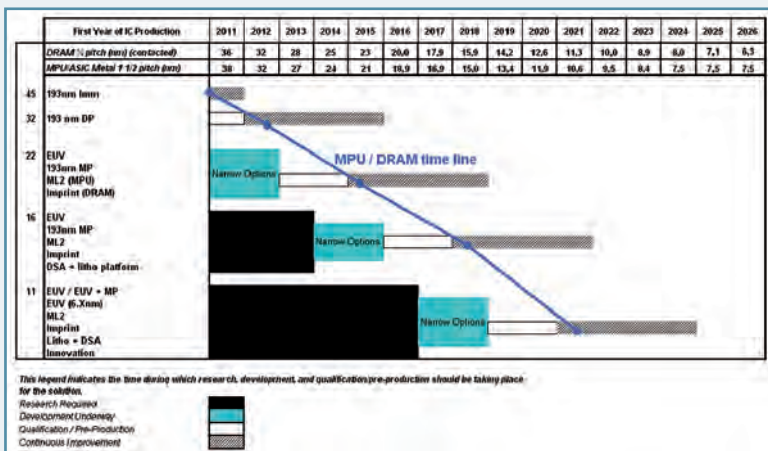

Figure 1. Lithography choices listed in the International Technology Roadmap for Semiconductors (ITRS, 2011)

EUVL works at an exposure wavelength of 13.5 nm, which is electromagnetic radiation absorbed at a high rate by nearly any solid material. Therefore, photomasks must be of reflective nature. This is accomplished by a Multi-layer structure deposited on top of a low-thermo expansion quartz substrate (LTEM substrate) (Figure 2).

Defect-free photomasks have always been a pre-requisite for high yields in Semiconductor device manufacturing. However, the fragile nature of the EUVL photomask multi-layer, is put-
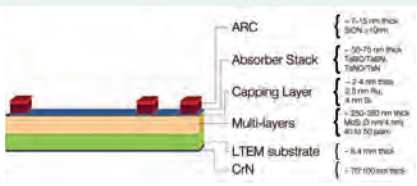

Figure 2. Structure of a EUVL Photomask (Source: SEMATECH)

ting forward new requirements for photomask cleaning. SUSS MicroTec as the leading provider of advanced photomask cleaning equipment is addressing these new challenges systematically, collaborating with leading captive and merchant photomask manufactures, device manufacturers as well as Semiconductor Research Institutes.

The use of MegaSonic agitation is a widely used phenomenon for particle removal in photomask cleaning. For the advanced technology nodes the problem of damaged sub resolution assist features (SRAF) became highly prevalent in 193i optical masks. EUV masks do not have SRAF structures yet and the smaller feature aspect ratio and stronger material interface makes the pattern robust to withstand higher MegaSonic energy. However Ru capping layer pitting as a result of MegaSonic cavitation is making the use of acoustic cleaning questionable for EUVL reticles. Figure 3.a compares the number of added pits from a 1MHz MegaSonic system on different EUVL reticle layers and figure 3.b shows an SEM image of a typical pit generated by MegaSonic. Ru surface is more prone to
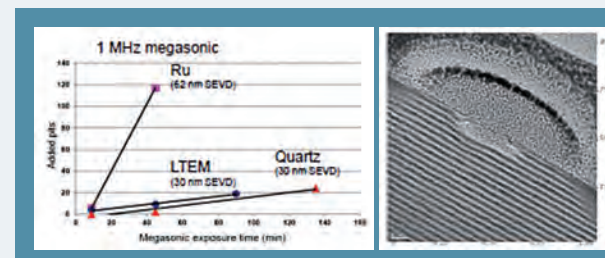

Figure 3. a) Plot showing Sematech's published data on a number of pits added on Ru, LTEM and Quartz substrates as a function of MegaSonic exposure time[2] b) SEM picture showing typical morphology of a Pit on an EUV mask surface[2]

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a)	
The Bubble Equation	$R\ddot{R} + \frac{3\dot{R}^2}{2} = \frac{1}{\rho}\left[\left(P_0 + \frac{2\sigma}{R_0} - P_V\right)\left(\frac{R_0}{R}\right)^\gamma + P_V - \frac{2\sigma}{R} - \frac{4\mu\dot{R}}{R} - P_0 - P_A\sin\omega t\right]$
Pressure Inside the Bubble	$P_i = P_0 + \frac{2\sigma}{R_0}$
Cavitation Threshold	$P_B = P_V + \frac{8\sigma}{9}\left[\frac{3\sigma}{2\left(P_0 + \frac{2\sigma}{R_0}\right)R_0^3}\right]$
Boundary Layer Thickness	$\delta_H = 0.16\left(\frac{v}{Ux}\right)^{\frac{1}{7}} \cdot x$
Drag Force	$F_D = 1.7009\,(3\pi\mu V d_p)$
Drag Moment	$M_D = 0.9439934\,(2\pi\mu V d_p^2)$

b) Property	Main Effect
Cavity Type (Vaporous or Gaseous)	• Cavitation Threshold
Gas Solubility	• Size of Cavity • Stability of Cavity
Gas Thermodynamic Properties	• Cp, Cv (Polytrophic index) • Size and Stability of Cavity
Media Thermodynamic Property	• Vaporous or Gaseous Bubbles
Media Viscosity	• Boundary Layer Thickness • Drag Force
Media Surface Tension	• Pressure Inside the Bubble • Cavitation Threshold

Table 1. a) The MegaSonic cavitation parameters and their dependence on media physical properties
b) The media properties and there effect on MegaSonic cavitation parameters [5, 14]

pitting as compared to LTEM and quartz[1, 2].

The acoustic energy transfer in MegaSonic systems can result into acoustic cavitation[3, 4]. Acoustic cavitation occurs due to the sinusoidal pressure variations that travel through the liquid along with the acoustic wave.
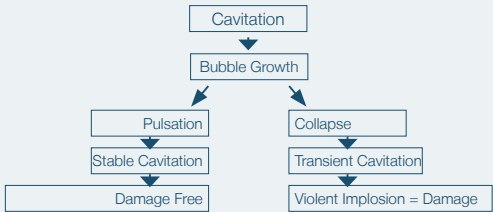

Figure 4. Schematic explaining the acoustic cavitation phenomenon created by MegaSonic energy in a liquid

During the low pressure component of the acoustic wave, small cavities form in the liquid which either compress or implode in the high pressure part of the propagating wave[5]. The presence of pulsating bubbles indicates stable cavitation. The implosion phenomenon is called transient cavitation (Figure 4).
Implosion of cavitating bubbles leads to localized high pressure and high temperature values which create shock waves in the liquid resulting not just in particle removal but also in feature damage and Ru pitting (Figure 5). In contrast, stable cavities can undergo large amplitude pulsations resulting into micro-streaming and such micro-streaming can lead to intense shear stresses along the boundary at the interface of cleaning media and photomask surface[6]. These shear stresses lead to drag forces and

rolling moments on particles on the photomask surface which subsequently overcome the adhesion force between particle and surface[7]. Since there are no shock waves generated, the chances for Ru pitting reduce significantly (Figure 5). It is obvious that stable cavitation can resolve the issue of Ru pitting or pattern damage. The cavitation bubble behavior is dependent on physical properties of the cleaning media. Table 1.a shows different equations on multiple cavitation parameters and each of these equations constitute physical property parameters of the liquid media. Table 1.b lists the effect of different media properties on cavitation behavior. Therefore it would be logical to conclude that media and gas physical properties are the main variables that define cavitation behavior and subsequent cleaning effect. If an appropriate cleaning media with optimized physical properties is chosen, it is feasible to generate predominantly stable cavitation.
Earlier SUSS MicroTec Photomask Equipment (former HamaTech APE) has published extensive research on the MegaSonic phenomenon where SRAF damage free cleaning is demonstrated[8-13]. In this study we applied the MegaSonic knowledge gained while solving SRAF damage issue
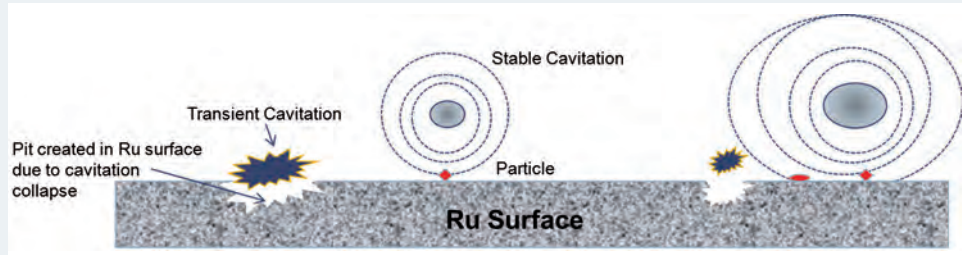

Figure 5. Schematic depicting the Ru pitting phenomenon as a result of transient cavitation events.

in 193i mask cleaning, to resolve the Ru pitting issue on the EUV mask cleaning. The gasses or vapours filled in the cavitation bubbles define the bubble wall movement or the pulsation of the bubble under propagating acoustic wave. This bubble wall movement defines the nature of the cavity, i.e. whether it would stay a stable pulsating bubble or whether it will collapse under acoustic pressure variations. The gas or vapour inside the bubble constitutes gaseous or vaporous state of the cleaning chemistry used during cleaning. Therefore it is important to ana- lyse the effect of cleaning chemistry on pattern damage and Ru pitting. We correlate the effect of liquid cleaning media on SRAF feature damage and Ru pitting.

2. EXPERIMENTAL
2.1 PROCESS PARAMETERS
All the pattern damage and Ru pitting tests were performed using the SMT PE MaskTrackPro (MTPro) mask cleaning tool. The process parameters were automatically monitored and controlled with a standard recipe programmed on the MTPro tool. DI water used for the tests was de-gassed before it was supplied to the cleaning chemical distribution system. Chemicals (NH_4OH or H_2O_2) and gases (CO_2 or H_2) were added into the de-gassed water to prepare the respective cleaning media. The cleaning media tested are: SC1 ($NH_4OH + H_2O_2 + DI$), $NH_4OH + H_2O$, $H_2O_2 + H_2O$, $H_2 + H_2O$, and a new cleaning Chemical A. These cleaning media are tested at different MegaSonic power values.

2.2 CHARACTERIZATION
Pattern damage induced by different MegaSonic cleaning process conditions was analyzed using a pattern mask inspection tool. Ru pitting was analysed using high sensitivity blank inspection tool. PRE was tested on deposited SiN particles on blank substrates. Absorber CD is measured on an EUV patterned mask using a CD-SEM tool and an actinic EUV-reflectometer is used for EUV-R measurements.

2.3 MATERIALS & METHODS
Ru pitting was tested on Ru-multilayer blanks. Pattern damage was tested using optical Phase Shift Masks (PSM) with Sub Resolution Assist Feature (SRAF) size suited for advanced tech- nology nodes. For this evaluation, an advanced mechanical feature of the MTPro was utilized, Focused Spot Cleaning (FSC)[15]. FSC allowed more than 20 different settings to be tested with only one test mask & Ru blank and a single inspection.

3. RESULTS & DISCUSSION
3.1 COMPARISON BETWEEN SC1 ($NH_4OH + H_2O_2 + DI$) & H_2-DI
Figures 6a & b compare the effect of SC1 and H_2-DI chemistries on pattern damage on 193i masks and Ru pitting on Ru blanks. It has been well known that H_2-DI if used at proper gas concentration shows lesser pattern damage than the SC1. NH_4OH has a very low boiling point (24.7°C, at 32%). Under acoustic conditions NH_4OH decomposes readily into NH_3 gas. H_2 gas has favourable cavitation properties as compared to NH_3 gas that fill the cavitation bubbles under MegaSonic. Moreover H_2 is intentionally dissolved into DI to create hydrogenated water, its bubbles provide cushioning effect for the acoustic energy transfer therefore pattern damage is reduced. A similar effect is observed on the Ru pitting. H_2-DI MegaSonic creates lesser pits on the Ru as compared to SC1.
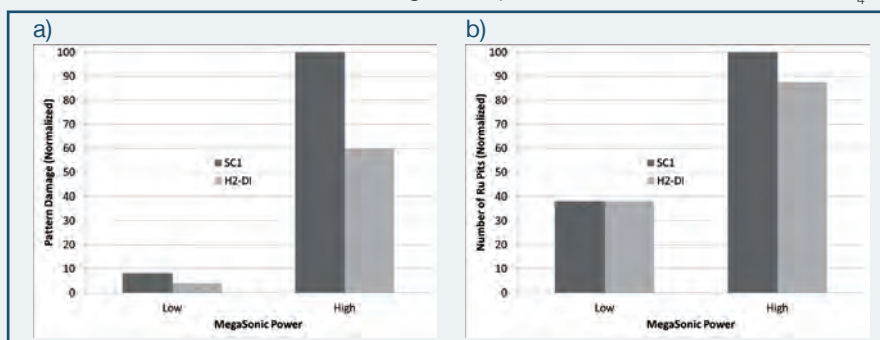
Figure 6. Comparison of cavitation and chemistry related effect of SC1 and H2-DI on a) pattern damage b) number of Ru pits.
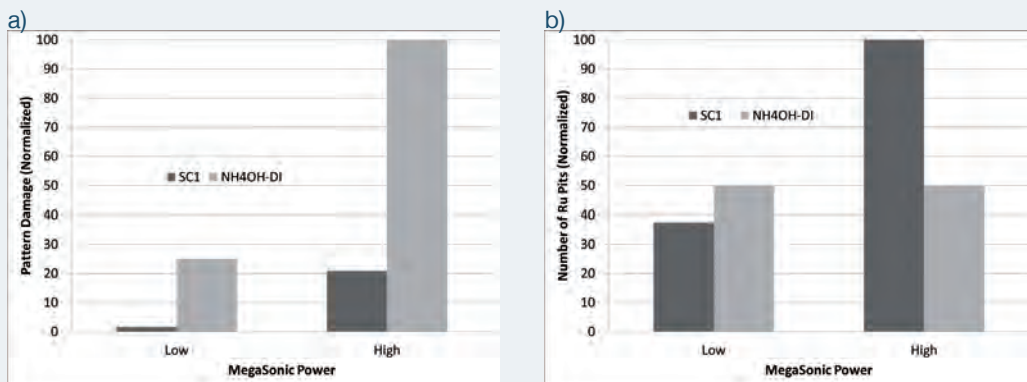
Figure 7. Comparison of cavitation and chemistry related effect of SC1 and NH4OH-DI on a) pattern damage b) number of Ru pits.

3.2 COMPARISON BETWEEN SC1 (NH_4OH + H_2O_2 + DI) & NH_4OH-DI

NH_4OH-DI shows much higher pattern damage than SC1 at both higher and lower MegaSonic power (Figure 7.a). However the number of pits produced from SC1 is higher than NH_4OH-DI at higher power (Figure 7.b). This discrepancy can be explained based on the physio-chemical phenomenon. SC1 is a mixture of NH_4OH-DI and H_2O_2 into DI-water. H_2O_2 is extremely oxidizing chemical and Ru surface is very prone to oxidation. H_2O_2 can react with Ru to form highly volatile Ru oxides (e.g. RuO_4). Therefore in case of MegaSonic SC1 treatment the cavitation damage is further enhanced by chemical reaction between H_2O_2 and Ru. At higher MegaSonic power the aggressiveness of the chemical attack increases because of stronger acoustic effects (localized pressure and temperature rise). This is why although the pattern damage is higher with ammonia; the number of pits added is higher with SC1. The pattern damage with SC1 is lower because some of the H_2O_2 can decompose into O_2 and O_2 in the cavitation bubbles has more favourable properties than the NH_3 gas. Decomposition of H_2O_2 ($2H_2O_2 \rightarrow 2H_2O + O2$) is thermodynamically favourable with a $\Delta H°$ of -98.2 kJ*mol^{-1} and a ΔS of 70.5 J*mol^{-1}*K^{-1}. High acoustic pressure and temperatures generated locally under the MegaSonic pressure waves may initiate such decomposition reaction.

3.3 COMPARISON BETWEEN NH_4OH - DI & H_2O_2-DI

To further verify the claims in section 3.2 above the pattern damage and Ru pitting comparison was made between the two main constituents of SC1, i.e. NH_4OH - DI & H_2O_2-DI (Figure 8.a & b). H_2O_2-DI alone has significantly lesser pattern damage than NH_4OH-DI alone. However as expected based on the discussion above the pitting was more severe with H_2O_2-DI at higher MegaSonic power. This confirms that H_2O_2's chemical reaction with Ru and significantly different cavitation properties of O_2 and NH_3 gas defines the pattern damage and Ru pitting behaviour. This also suggests that the process conditions that show lesser pattern damage do not necessarily produce lesser pitting on Ru surface. Physio-chemical effects of cleaning media used with MegaSonic have to be taken into account for effective process development.
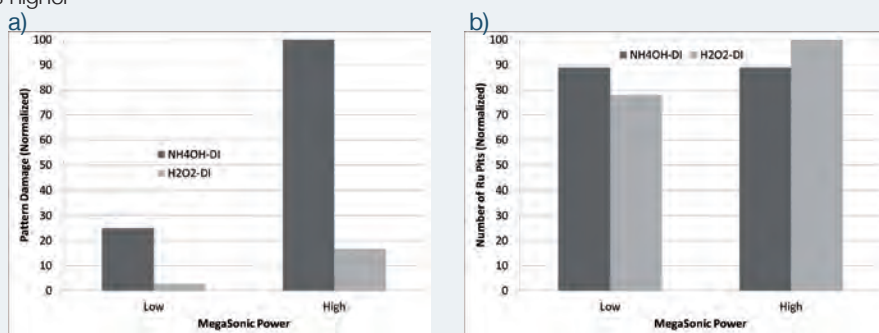

Figure 8. Comparison of the cavitation and chemistry related effect of NH_4OH-DI & H_2O_2-DI on a) pattern damage b) number of Ru pits
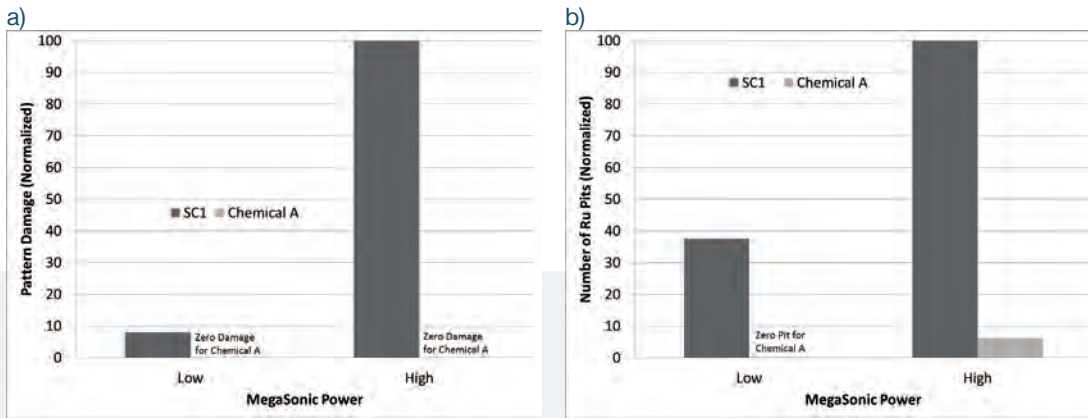
Figure 9. Comparison of the cavitation and chemistry related effect of SC1 and chemical A on a) pattern damage b) number of Ru pits.

3.4 COMPARISON OF SC1 ($NH_4OH + H_2O_2 + DI$) & NEW MEDIA (CHEMICAL A)

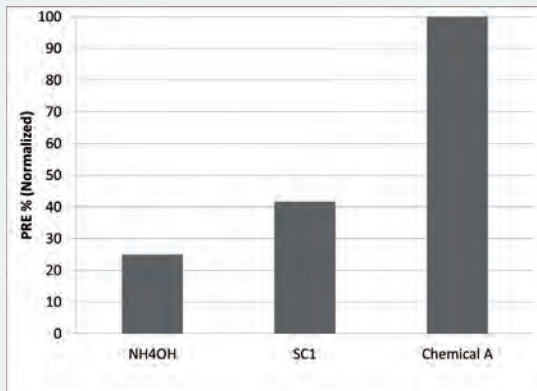As discussed earlier in section 3.1 to 3.4, the chemical nature of the cleaning media defines the cavitation behaviour in MegaSonic and physio-chemical behaviour in Ru pitting. Considering this, we have developed a new chemistry "chemical A" which has highly favourable cavitation behaviour and negligible chemical side-effects. Figure 9.a & b compares the effects of SC1 and Chemical A on pattern damage and Ru pitting.

Chemical A showed no pattern damage on any power level tested. Chemical A produced zero pits at lower MegaSonic power. At higher Mega-Sonic power, relatively insignificant number of pits is seen.

Since these tests were intentionally done at accelerated conditions, the MegaSonic process conditions were optimized further for zero Ru pit conditions using chemical A as part of the POR for mask cleaning.
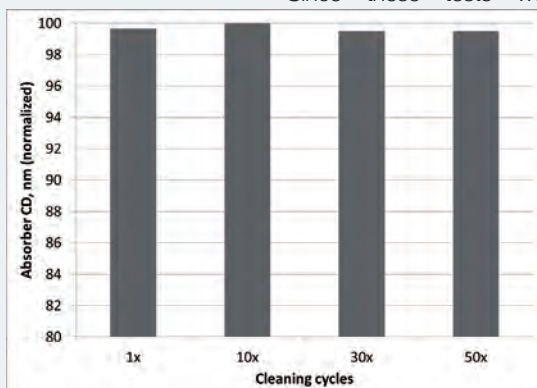

Figure 10. Particle Removal Efficiency (PRE) comparison between NH_4OH-DI, SC1 and Chemical A based Process of Record (POR).

Figure 11. Absorber CD changes as a result of multiple cleaning cycles of Chemical A based Process of Record (POR).

3.5 PRE COMPARISON OF SC1 ($NH_4OH + H_2O_2 + DI$) & NEW MEDIA (CHEMICAL A) USING COMBINATION NOZZLE

A complete Process of Record (POR) based on Chemical A was developed for the cleaning of EUVL reticles. The Particle Removal Efficiency (PRE) was compared between POR's based on NH_4OH-DI, SC1 & Chemical A (Figure 10). The PRE was tested while implementing combination nozzle (new hardware feature from SUSS MicroTec Photomask Equipment). In this new feature the reticle substrate is exposed to MegaSonic beam rinse and droplet spray simultaneously. While acoustic energy from MegaSonic beam dislodges particles from deep trenches, spray droplets provide additional lateral forces through jetting. Chemical A based POR was identified to achieve ~60% higher PRE as compared to SC1 based POR. The PRE for SC1 based POR is ~15% higher than NH_4OH-DI based process. Chemical A based POR shows no pattern damage and zero Ru pitting and has the maximum particle removal efficiency (PRE).

3.6 ABSORBER CD SHIFT

Figure 11 shows the effect of multiple cleaning cycles on absorber CD (Critical Dimension) changes using Chemical A based POR. The normalized CD is compared and plotted after 1x, 10x, 30x and 50x cleaning cycles. A CD increase of 0.35 nm (.035 nm/clean) was observed after first 10x cycles. However for subsequent cleaning cycles the CD was again stabilized to the original values. The random CD increase after first 10x cleaning can be attributed to CD-SEM's tool measurement artifact[16].

THE AUTHORS

Dr. SherJang Singh is working with SUSS MicroTec Inc., USA (former HamaTech Inc.) since 2006. He holds a Masters & PhD in Materials Sciences & Engineering from University of Cincinnati, Cincinnati, OH, USA. Dr. Singh started his career with SUSS as an onsite project engineer at Sematech Albany's EUV Mask Blank Development Center (MBDC) and is currently responsible for several mask cleaning R&D projects within the global R&D team. He is undertaking collaborative research with consortiums & major semiconductor manufacturers in the area of emerging lithography reticles. He has authored and co-authored ~20 research papers in Mask Cleaning and showcase SUSS's R&D efforts at multiple Mask & Lithography conferences every year. While at SUSS: He is a co-inventor on 1 issued and 1 pending patent on advanced mask cleaning methodologies.

Uwe Dietze has been with SUSS MicroTec Photomask Equipment (formerly HamaTech APE) since 1990 in various functions of customer service, sales and management. He is holding a Bachelor of Science Degree in Mechanical Engineering and has gained 32 years of experience in photomask and semiconductor technology. As Senior Director Surface Technology Innovations he is today responsible for the development of advanced features and technologies for SUSS wafer and photomask processing equipment.

Dr. Peter Dress is with SUSS MicroTec Photomask Equipment (former HamaTech APE) since 1998 based in Sternenfels, Germany. During his career at SUSS MicroTec he is holding various positions in process technology and equipment development. As Director Advanced Process Development he is now responsible for the worldwide process technology development addressing photomask and wafer coat, bake, develop, wet-etch, and clean technology. He studied Physics at Duisburg University, earning a diploma in 1993 and his PhD in 1998. In parallel he studied business administration at the University Hagen finished with a Pre-diploma in 1997. While doing his PhD studies he worked as Software Engineer at NeuroTech GmbH, a company in the printing industry.
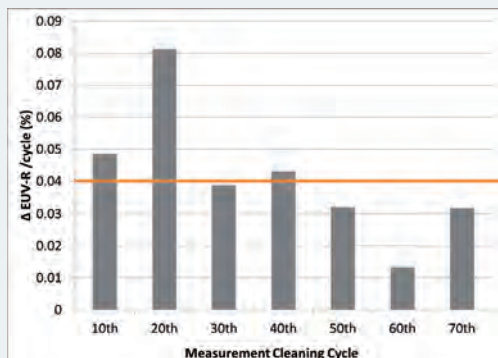
Figure 12. Plot showing effect of number of cleaning cycles on Ru-multilayer EUV- reflectivity

3.7 RU EUV-REFLECTIVITY

Since it is expected that an EUV reticle will be cleaned approximately 100 times in its lifetime, we tested Ru capping layer durability with chemical A based POR over 70x cleaning cycles. Figure 12 shows the effect of cleaning cycles on absolute EUV-reflectivity plotted every 10x consecutive cleaning cycles. The total change in absolute EUV-R after 70x cycles was found to be only 0.04% per clean (averaged over 70x cleans). An EUV-R increase was observed.

4. CONCLUSIONS

The process conditions that create pattern damage on 193i reticles do not necessarily create Ru pits on the EUVL reticles. Physio-chemical effects of cleaning media used with MegaSonic have to be taken into account for effective process development. The chemical nature of the cleaning media defines the cavitation behaviour in MegaSonic and physio-chemical behaviour in Ru pitting. Chemical A based POR shows no pattern damage and zero Ru pitting as compared to SC1 and NH_4OH-DI and has the maximum particle removal efficiency. This new process did not show any absorber CD shift over 50x clean and only showed an EUV-R change of 0.04% per cleaning cycle averaged over 70x cleans.

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