

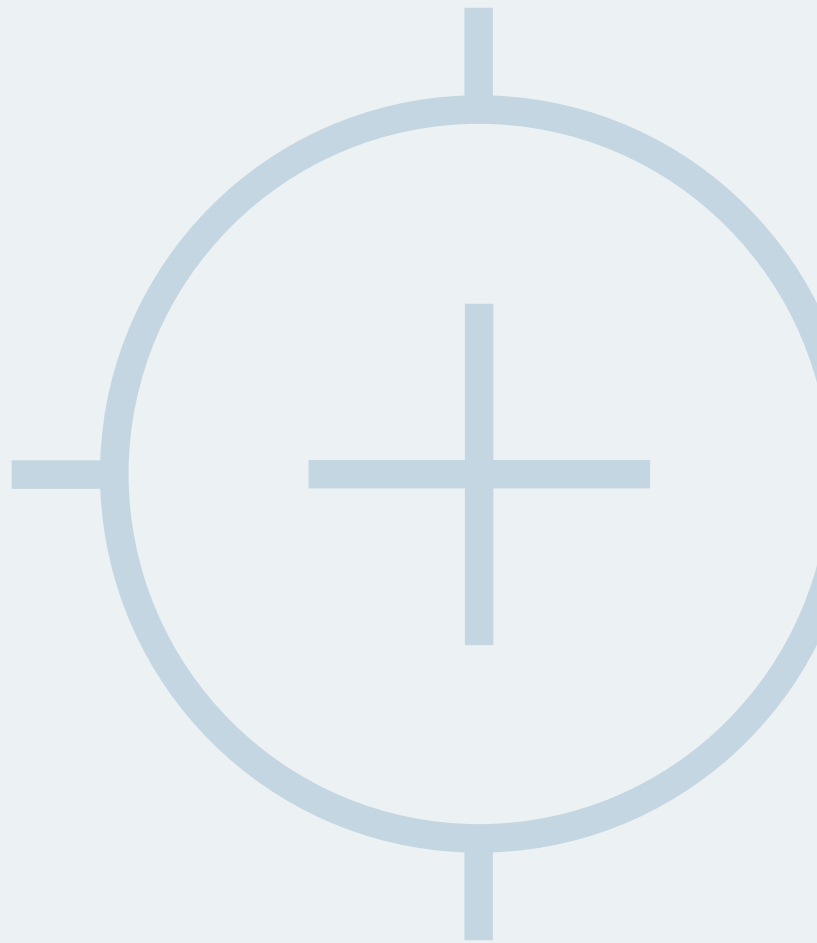
EFFICIENT OZONE, SULFATE AND AMMONIUM FREE RESIST STRIPPING PROCESS

Davide Dattilo

SUSS MicroTec Photomask Equipment GmbH & Co. KG | Germany

Uwe Dietze

SUSS MicroTec Inc. | USA



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Davide Dattilo SUSS MicroTec Photomask Equipment, Ferdinand-von-Steinbeis-Ring 10, 75447 Sternefelds, Germany
Uwe Dietze SUSS MicroTec Inc., 430 Indio Way, Sunnyvale, CA 94085, USA

1. INTRODUCTION

Conventional resist strip processes employ a variety of steps geared towards highly effective removal of organic and inorganic contamination from the mask surface.

Figure 1 summarizes the process steps in mask cleaning and the mostly used chemistries employed in 193i mask cleaning.

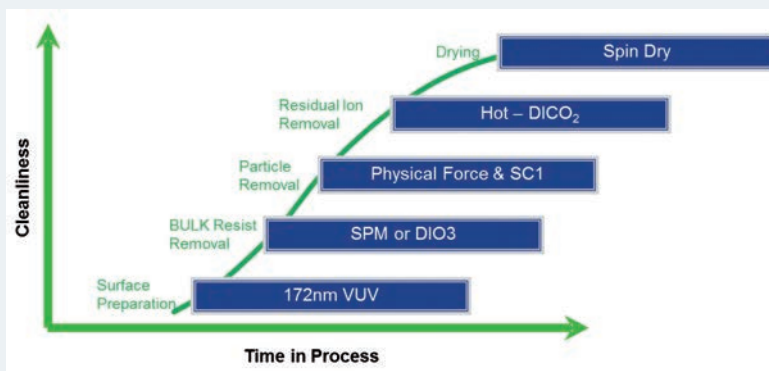


Figure 1. Principle sequence of a photomask cleaning process illustrating the increasing cleanliness of the photomask with progressing process time.

For proper wetting of the photomask surface with cleaning chemicals, higher surface energy is desired. A photomask surface is needed to be in hydrophilic state prior to the application of wet chemistries. Hydrophilic surfaces promote better liquid distribution and uniform chemical effects across the surface; as part of the POR cleaning process flow a 172nm excimer VUV step was

used to achieve a low water contact-angle on the surface. The UV radiations under the oxygen atmosphere create oxygen radicals leading to surface organic bond cleavage as well as direct surface activation for better wetting^[8,9]. However, the high energy radiations exposure of the photomask surface may also cause interface stress or material diffusion, which eventually transforms into unpredictable mask registration shifts. Ozone water (DIO₃) or conventional SPM (H₂SO₄ + H₂O₂) was used for resist stripping and organic removal, however haze formation^[10,11] or oxidative degradation of photomask materials^[12,13] has been observed as a result of the very high oxidation potential of Ozone and Sulfate ions getting trapped on the surface and reacted with ammonium ions used in the following process steps. Such material damage can affect optical properties of the materials and can also cause CD shift.

APM (dilute NH₄OH + H₂O₂) chemistry is typically used with MegaSonic agitation for particle removal. For the advanced technology nodes the problem of damaged sub resolution assist features (SRAF) is highly common in 193i optical masks. The acoustic energy transfer in MegaSonic systems can result into acoustic cavitation^[14, 15]. Acoustic cavitation occurs due to the sinusoidal pressure variations that travel through the

liquid along with the acoustic wave. During the low pressure component of the acoustic wave, small cavities form in the liquid, which can implode in the high pressure part of the propagating wave^[16]. This implosion phenomenon is called transient cavitation. Implosion of cavitating bubbles leads to localized high pressure and temperature values which create shock waves in the liquid resulting not just in particle removal but also in feature damage, hence transient cavitation must be avoided. Instead stable cavities must be promoted, which can undergo large amplitude pulsations without implosion, resulting into micro-streaming and such micro-streaming can lead to intense shear stresses along the boundary^[17]. These shear stresses lead to drag forces and rolling moments which subsequently overcome the adhesion force between particle and surface^[18]. Since there are no shock waves generated, the chances for Ru pitting reduce significantly.

The cavitation bubble behavior is dependent on physical properties of the cleaning media. The gas 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 it will collapse under acoustic pressure. The gas or vapour inside the bubble constitutes gaseous or vaporous state of the cleaning chemistry used during cleaning. If an appropriate cleaning media with optimized physical properties is chosen, it is feasible to generate predominantly stable cavitation.

A hot water rinse with DI-water at temperatures around 80°C is used as a standard approach to reduce the residual ion level on the photomask surface. This process has limitations pertaining to intrinsic cleanliness of the DI-water at elevated temperatures above 70°C (particle adders from heating systems)^[19]. Moreover there is temperature drop during Hot-DI transfer from heater system to point of use (photomask surface), which significantly reduces the temperature

below 80°C and diminishes the ion removal capability.

In this paper sulfate and ammonium free new chemistries and techniques are presented to overcome the described drawbacks arising from:

- 1) UV exposure during surface preparation;
- 2) Oxidizing agents exposure during bulk resist removal;
- 3) Transient cavitation exposure of sub-nano meter features during particle removal;

The presented alternative approaches are shown in Figure 2.

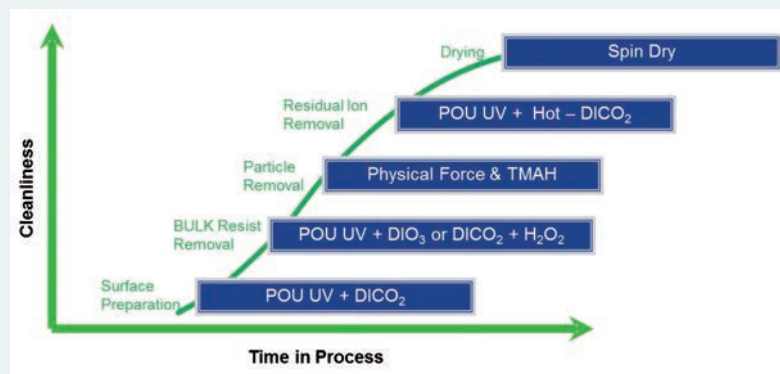


Figure 2. Modified sequence of a photomask cleaning process: direct UV absorption or UV mediated photo-chemical products are used for surface conditioning and bulk resist removal. Physical force cleaning has been modified with TMAH as alkaline chemical.

172 nm UV photochemistry has been replaced by 185 nm or 254 nm UV chemistry for surface conditioning; experimental results show that the contact angle can be efficiently tuned to hydrophilic by direct exposure of the surface to longer wavelength UV-light.

Photolyzed ozone or hydrogen peroxide is here presented as a valid alternative to SPM or DI-O3 to accomplish bulk resist removal.

Finally, TMAH chemistry is presented as alternative to ammonium hydroxide chemistry to induce more stable cavitation thus allowing to SRAF preservation and pattern durability.

Figure 3 illustrates the two different possible approaches to run photo-chemically driven cleaning processes;

254nm UV-light is directly absorbed by organic

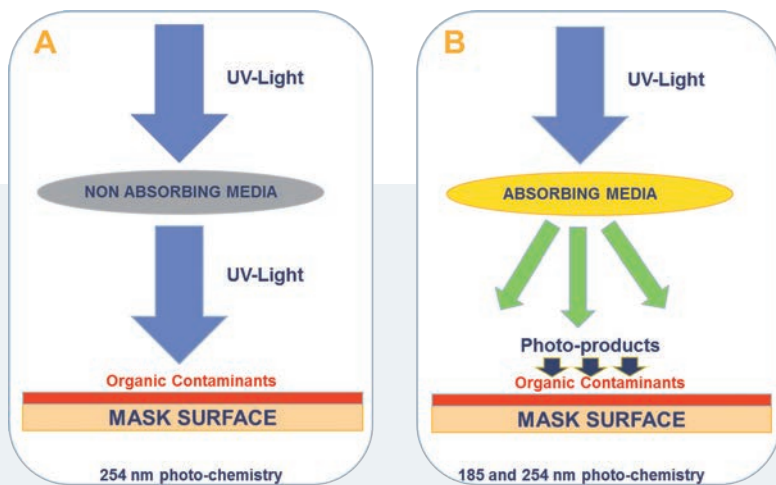
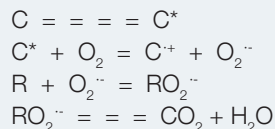


Figure 3. Direct 254 nm UV light absorption in presence of non-absorbing media (A); photolysis of absorbing media leading to photo-products which in turn attach organic molecules and degrade them (B).

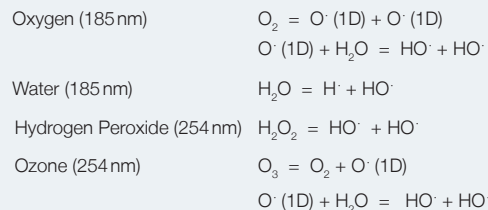
contaminants in presence of non-absorbing media leading to crust resist removal or surface conditioning (Figure 3A). At 254 nm organic molecules have a maximum absorption which is bringing the Carbon atoms in their excited state (C^*); an electron transfer to molecular Oxygen leads to radical Oxygen anion that attacks the organic molecule radicals R to lead to Peroxyl radicals ($RO_2^{\cdot-}$), that undergoes to consecutive oxidation reactions to CO_2 and water. This reaction scheme can be summarized as follows^[6]:



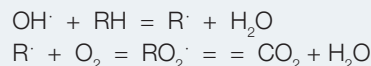
Each of these radical reactions competes with recombination; however the intensity of the supplied light ensures enough radical concentration to get to organic oxidation to carbon dioxide and water.

Absorption can also take place on metal or silica (SiO_2 , glass or quartz) surfaces often leading to thin oxide layers resulting in a more polar, i.e. hydrophilic surface.

In the presence of absorbing media, such as Ozone (O_3), Oxygen (O_2) or Hydrogen Peroxide, the absorption of UV light leads to photo-products which in turn attach the organic (resist) molecules on the surface (Figure 3B). 254 nm or 185 nm emissions from medium and low pressure Mercury lamps can be selectively used to photolise these chemicals. At these wavelengths such media (Oxygen, Water, Ozone, Hydrogen Peroxide) lead to photolysis, with generation of highly reactive singlet Oxygen ($O(1D)$) and Hydroxyl radicals^[20]:



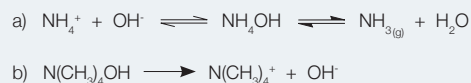
Hydroxyl radicals are usually responsible for organic removal from the surface; the reaction mechanism is known as hydrogen abstraction and produces organic radicals R, which in turn attach molecular oxygen to lead to Peroxyl radicals that undergo consecutive oxidation reactions to water and carbon dioxide:



Megasonic clean is here presented with the modification of the alkaline chemistry, which typically employed ammonium hydroxide for this purpose; TMAH is a valid alternative to this chemistry for several reasons:

- 1) Respect to ammonium hydroxide is a strong base, thus totally dissociated in ions when put in water, leading to favorable pH and Zeta Potential with much smaller used amounts, thus leading to higher PRE;
- 2) Ammonium Hydroxide exist in equilibrium with dissolved gaseous ammonia (NH_3) leading to transient cavitation as previously reported^[7]

Scheme 1 summarizes the involved equilibria in solution.



Scheme 1. Dissociation and decomposition behavior of Ammonium Hydroxide and TMAH; a) Partial dissociation of NH_4OH as weak base ($pK_b = 4.75$) and its equilibrium with ammonia (NH_3) and water; b) complete dissociation of TMAH as strong base into tetramethyl ammonium cation and hydroxides.

Molecular symmetry plays also an important role; the bigger positive ions of TMAH molecules prevent etching into Silicon or Molybdenum^[21]; Figure 4 shows the different dimensions of NH_4^+ and $N(CH_3)_4^+$ ions.

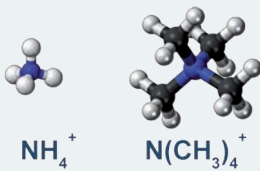


Figure 4. Cation sizes for NH_4^+ (ionic size 1.43 Å) and $\text{N}(\text{CH}_3)_4^+$ (ionic size 2.51 Å)

2. EXPERIMENTAL

2.1 PROCESS PARAMETERS

All the tests were performed using the SUSS MaskTrackPro (MTPPro) mask cleaning tool. The process parameters were automatically monitored and controlled with a standard recipe programmed on the MTPPro tool. DI water used for the tests was de-gassed before it was supplied to the cleaning chemical distribution system. Chemicals (TMAH or H_2O_2) and gases (CO_2) were added into the de-gassed water to prepare the respective cleaning media. The cleaning media tested are: SC1, TMAH, Ozone.

2.2 CHARACTERIZATION

Strip rates were measured by measuring photoresist coated before and after the process. Pattern damage was tested using optical Phase Shift Masks (PSM) with Sub Resolution Assist Feature (SRAF) size suited for advanced technology nodes. For this evaluation, an advanced mechanical feature of the MTPPro was utilized, Focused Spot Cleaning (FSC)^[10]. Acoustic energy was measured using a handheld acoustic sensor meter. PRE was tested on deposited SiN particles on blank substrates. PSM mask CD is measured using a CD-SEM tool. Phase and Transmission loss based on TMAH POR (Process of Record) is compared with conventional POR.

3. RESULTS & DISCUSSION

3.1 SURFACE CONDITIONING

172 nm UV exposure was replaced with DI- CO_2 water treatment upon 254 nm exposure from Mercury lamp. 1, 2 and 3 minutes of exposure of Chromium surfaces efficiently decrease the contact angle to $<5^\circ$, thus leading to a very hydrophilic surface. Results are summarized in Figure 5. The milder photochemical conditions

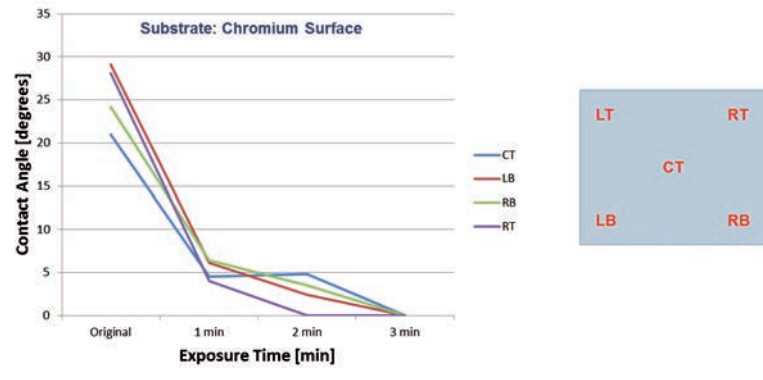


Figure 5. Treatment of Chromium Surface to 1, 2 and 3 minutes of UV-light in combination with DI- CO_2 ; exposure times longer than 2 minutes bring the contact angle to zero.

(longer wavelength) ensure damage preventing on the metal surface.

3.2 RESIST CRUST REMOVAL

The described direct photochemical approach (Figure 3A) has been used for crust resist removal; to prove that a photoresist spin coated mask blank was exposed to DI- CO_2 in presence of 254 nm UV light; the results are shown in Figure 6. Highly hydrophobic resist surfaces are turned into more hydrophilic thus indicating efficient crust resist removal.

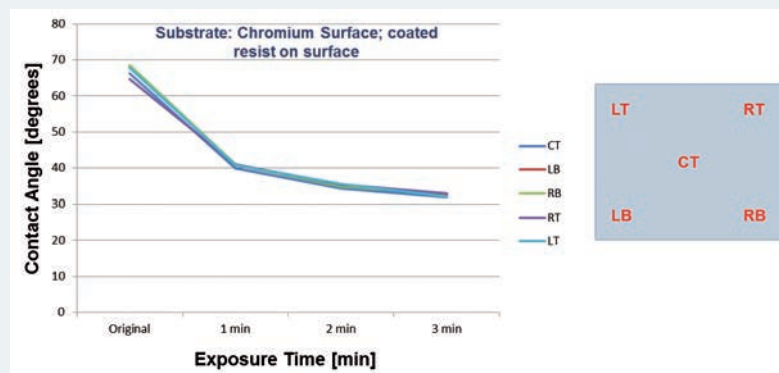


Figure 6. Treatment of resist coated Chromium surface to 1, 2 and 3 minutes of UV-light in combination with DI- CO_2 ; the decrease in contact angle reaches about 40 degrees.

3.3 BULK RESIST REMOVAL

Efficient Ozone or Hydrogen Peroxide decomposition under UV light (254 nm or 185 nm) is used for bulk resist removal. A resist coated mask was partially scanned under IUV conditions to evaluate strip rates also in the non-scanned areas, i.e. stripping from any un-decomposed Ozone or Hydrogen Peroxide. The process parameters are optimized to have minimum strip rate in the non-scanned area of the mask and maximum rate in the scanned regions. The stripping results are summarized in Figure 7.

Several process parameters have been chan-

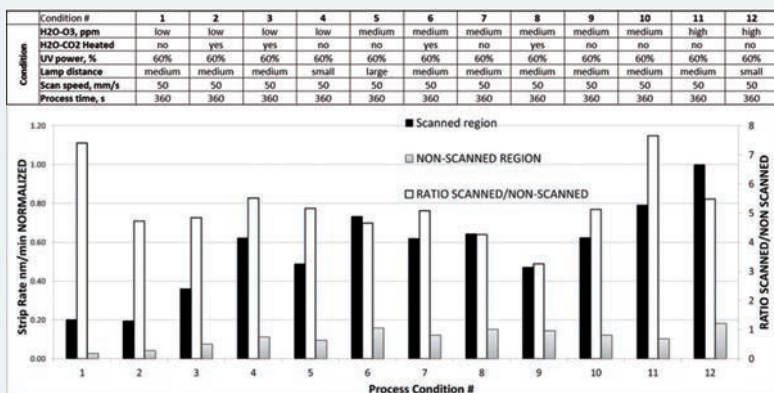


Figure 7. Stripping results obtained by photolysis of absorbing media (such as Ozonated water); stripping in the non-scanned regions of the surface indicate damage risk due to un-decomposed oxidizing agents. Low ratios scanned to non-scanned regions in parallel with good strip rate in the scanned regions indicate good process conditions.

ged to find the best stripping conditions which should coincide with high scanned to non-scanned regions ratios and high absolute strip rate in the scanned regions.

3.4 PARTICLE REMOVAL

The described TMAH chemical benefits have been demonstrated in terms of SRAF preservation, risk of Ruthenium pitting, particle removal efficiency and CD shift. TMAH has been tested alone and in combination with H₂O₂. Typically SC1 and NH₂OH-DI show higher PRE than H₂-DI as well as better CD shift, therefore in this study TMAH and TMAH + H₂O₂ were compared with SC1 in terms of PRE and CD shift. These results are shown in Figure 8. TMAH chemistry gives

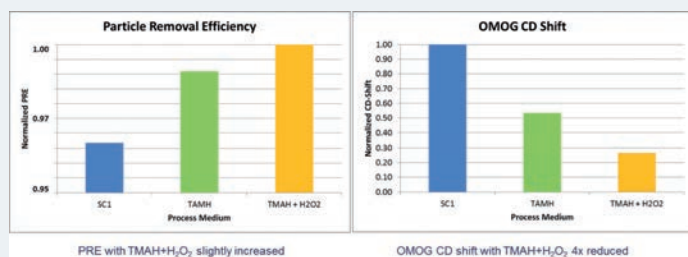


Figure 8. Left: PRE comparison between SC1 and TMAH and TMAH + H₂O₂; the latter chemistry provides the higher PRE. Right: OMOG CD shift comparison between SC1 and TMAH and TMAH + H₂O₂; the latter chemistry provides higher reduction of CD shift.

significantly higher PRE as compared to SC1. This higher removal efficiency is attributed to higher pH and higher zeta potential as discussed in the introduction above. TMAH and its combination with H₂O₂ have also been compared to SC1 in terms of SRAF preservation and risk of Ru pitting; the results are summarized in Figure 9.

The shown improved SRAF preservation and lower Ruthenium damage risk is explained by better cavitation control due to the elimination of gaseous ammonia (NH₃) as described above.

4. SUMMARY

In this paper the cleaning process has been discussed with possible drawbacks arising from highly oxidising agents and not favour-

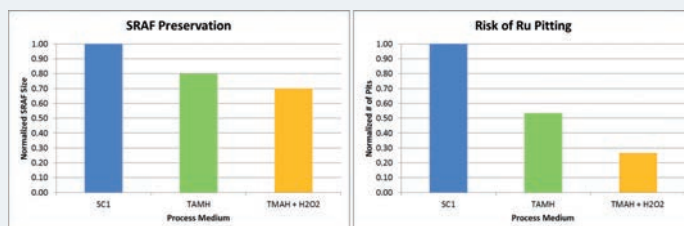


Figure 9. Left: SRAF preservation comparison between SC1 and TMAH and TMAH + H₂O₂; TMAH and TMAH + H₂O₂ preserve SRAF of smaller size. Right: Risk of Ruthenium pitting comparison between SC1 and TMAH and TMAH + H₂O₂; TMAH and TMAH + H₂O₂ also reduce risk of Ru Pitting.

able chemistries for cavitation during physical force cleaning. An alternative sulphate and ammonium free process is here proposed and discussed. The results show that surface preservation is possible by replacing SPM by In-situ UV photolyzed Ozone or Hydrogen Peroxide; moreover, replacement of Ammonium Hydroxide with Tetramethylammonium Hydroxide (TMAH) favourably influences cavitation properties leading to reduced feature damage in FRAS 193i photomasks. The elimination of Sulphate and Ammonium also prevents haze formation typically due to the combination SPM and APM chemistries.

THE AUTHORS



Davide Dattilo took his master degree in Chemistry in 2000 and his PhD in Molecular Materials in 2004.

He gained experience in Surface Chemistry during his 3 years post-doc at the University of Padova, where he studied the basic reactivity of crystalline substrates such as Silicon and Gold.

He worked for 5 years in the R&D department of Molecular Stamping, a bio tech company where he has been responsible of the development of Surface Chemistry for the immobilization of organic molecules on solid substrates and passivation approaches. Since 2012 he is Process Scientist at SUSS MicroTec Photomask Equipment leading R&D projects for cleaning of optical and EUV photo-masks.



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.

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