



› **CHEMISCHE REINHEID VAN
PRODUCTEN**

Ing. F.T. Molkenboer

TNO innovation
for life

INHOUDSOPGAVE

- › **Wat is chemische reinheid, definitie en voorbeelden van werkgebieden waar chemische reinheid essentieel is voor het goed functioneren van een systeem**
 - › Definitie chemische reinheid
 - › Lithografie
 - › Inspectieapparatuur
 - › Aardobservatie / Ruimtevaart
- › **Plan van aanpak vanuit een praktijkvoorbeeld**
 - › Opstellen van eisen
 - › Realisatie van eisen
 - › Valideren van eisen
- › **Conclusie**

WAT IS CHEMISCHE REINHEID

- › Chemische vervuiling is
 - › Any substance in or on the surface that can, by its chemical nature, adversely effects the product, process or equipment

- › Chemische vervuiling kan optreden door
 - › Moleculaire vervuiling (b.v. koolwaterstoffen (vetten), water en zuurstof, ...)
 - › Deeltjes vervuiling (organisch, in-organisch)
 - › Vervuiling in het bulkmateriaal dat vrijkomt
 - › Interactie van bulkmaterialen met processen in het vacuüm



E 1235 – 08

3.1.6 *contaminant, n*—unwanted molecular and particulate matter that could affect or degrade the performance of the components upon which they reside.

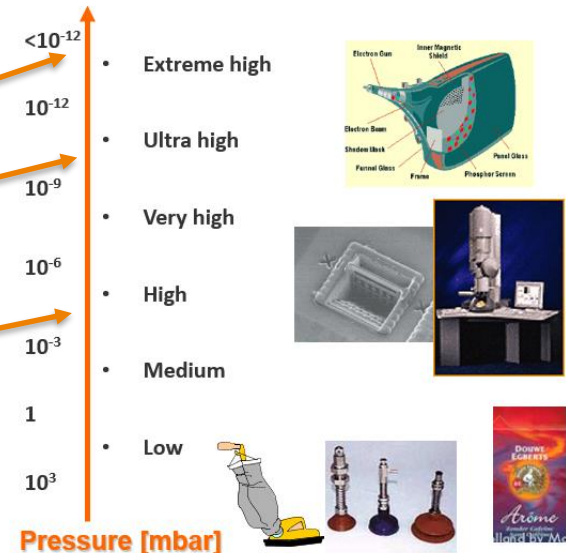
VACUÛM

- › Een vacuüm is een ruimte zonder materie en zonder druk [wikipedia]
 - › In praktijk is een ruimte zonder druk en materie niet haalbaar
 - › 10^{-12} mbar heeft nog steeds 10^5 moleculen per cm^3
 - › 10^{-6} mbar geeft 1 monolaag aangroei per seconde

- › Vacuüm heeft vele toepassingsgebieden
- › In “big science” vanaf high vacuüm
 - › CERN en op de maan

- › SEM

- › TL lamp



EUV LITHOGRAFIE

- › Steeds kleinere microchips, met nieuwe lithografiemethode



Foto: ASML

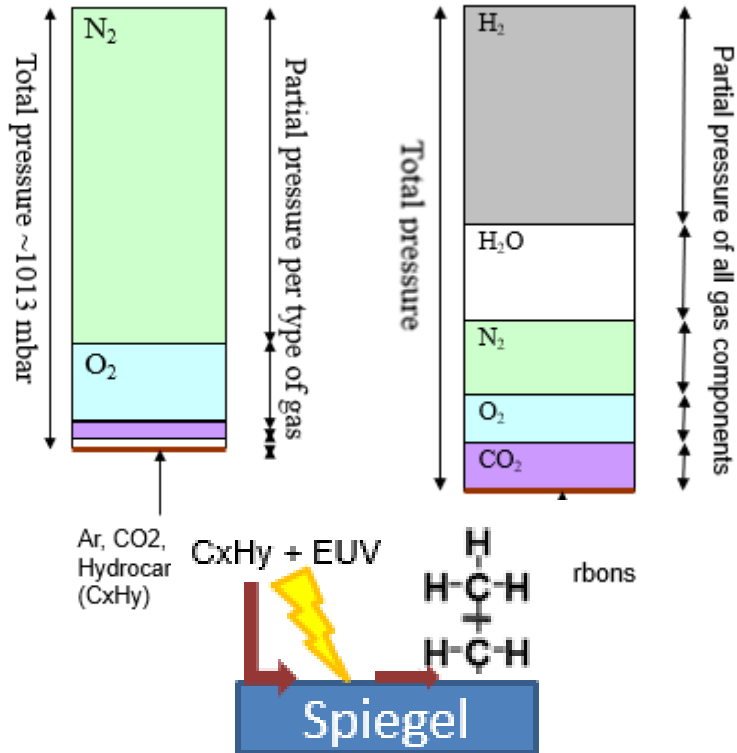
- › EUV lithografie
- › Golflengte: 13,5 nm
- › In ultra-schoon vacuüm
- › Spiegels in plaats van lenzen



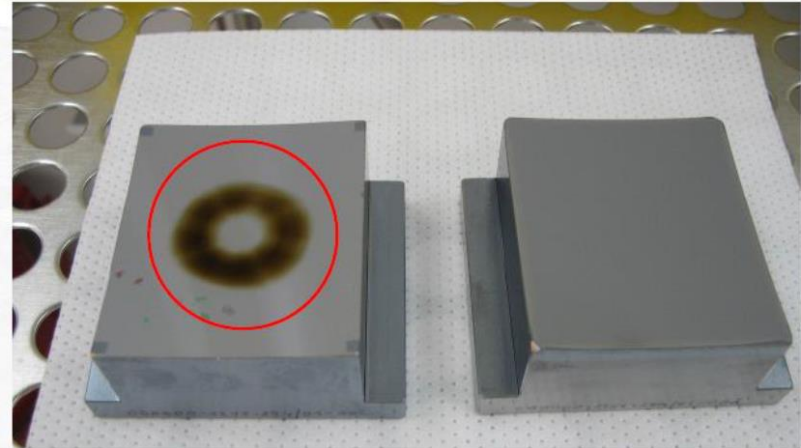
Foto: Carl Zeiss SMT

Contamination = decreased reflectivity

EUV LITHOGRAFIE



Contamination on illumination optics mirror N1 (old vs. new)

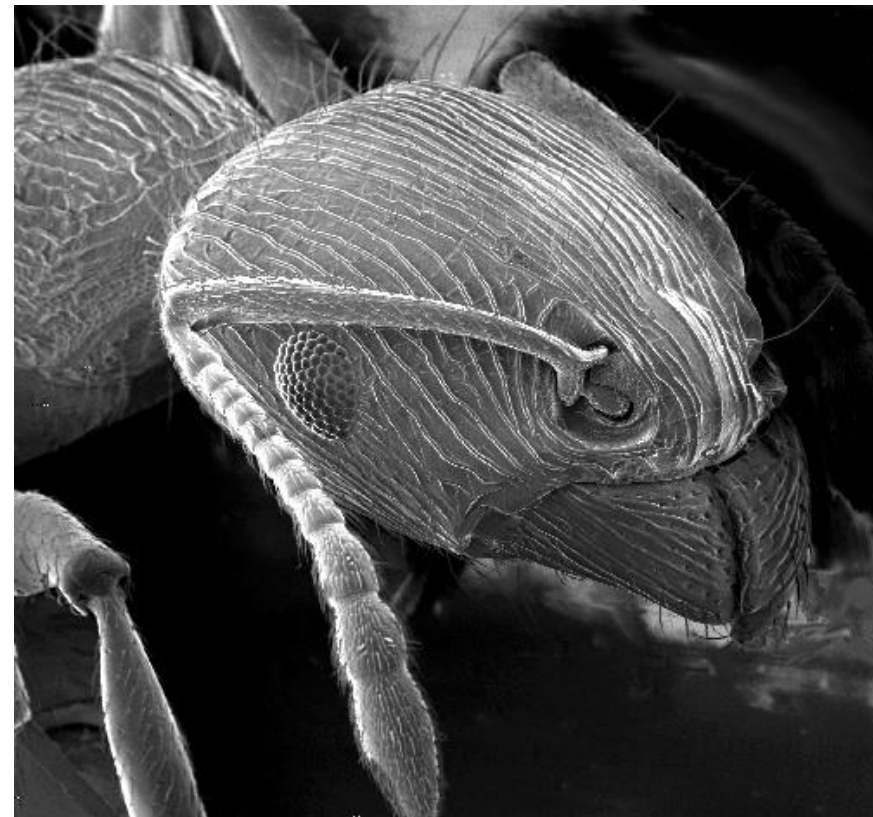
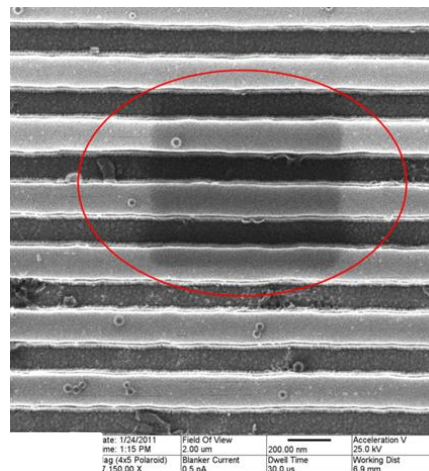
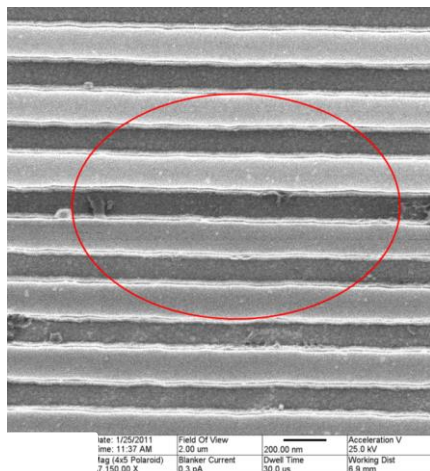


NIST
National Institute of Standards and Technology
U.S. Department of Commerce

Intel
Bron: A plan to measure EUV resist contamination in the presence of hydrogen: Robert Berg (NIST) et al.: 2015 International workshop on EUV lithography, Maui, Hawaii

INSPECTIEAPPARATUUR

- › Scanning Electron Microscopy (SEM)
- › Transmission Electron Microscopy (TEM)
- › Focus Ion Beam (FIB)

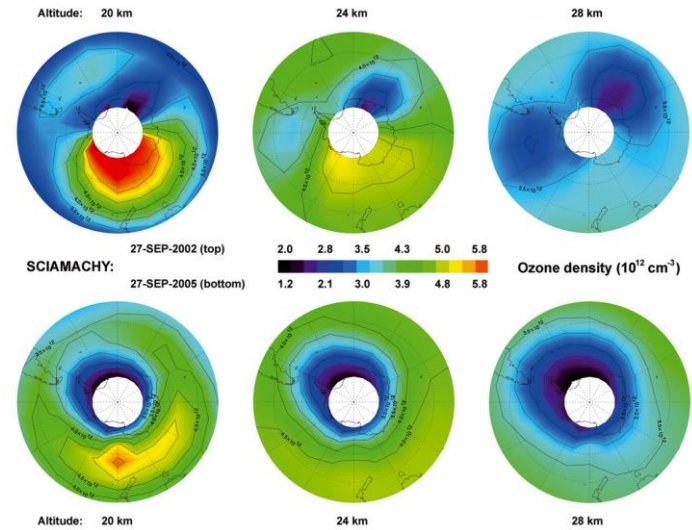
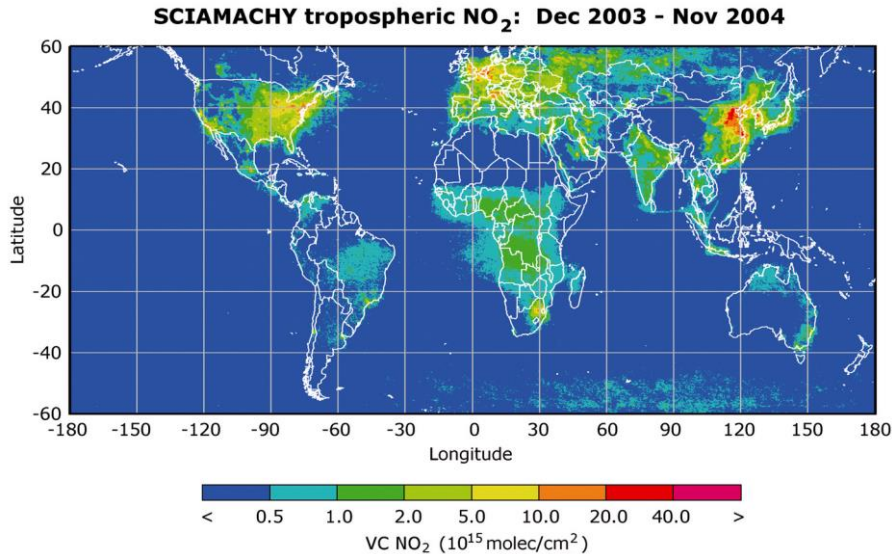
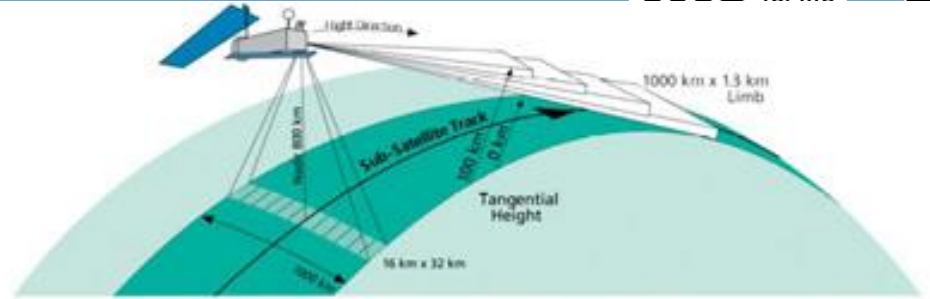


<http://usgsprobe.cr.usgs.gov/picts.html>

AARDOBSERVATIE

› Sciamachy

- › Kijkt naar verschillende gassen in de atmosfeer

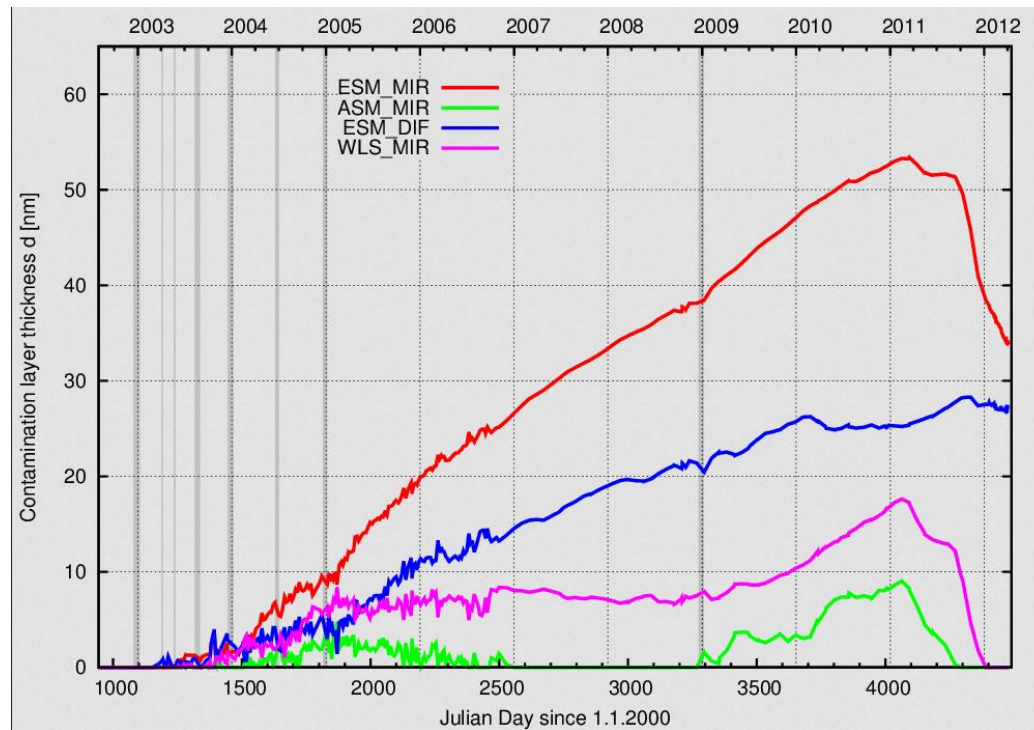


https://atmos.eoc.dlr.de/projects/scops/sciamachy_book/sciamachy_book_figures/chapter_10_figures.html

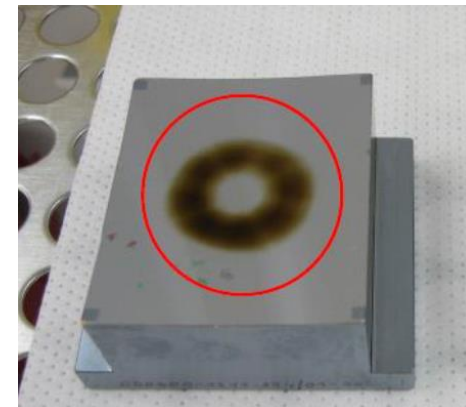
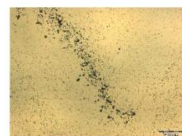
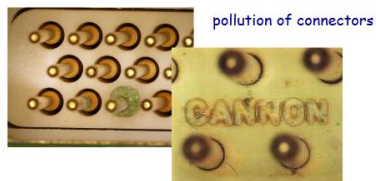
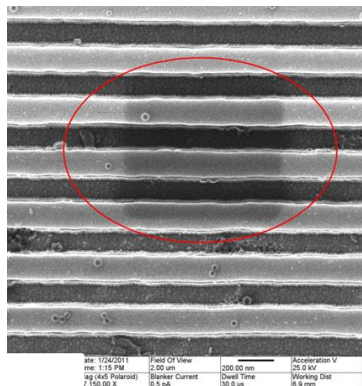
AARDOBSERVATIE

› Sciamachy

<http://www.iup.uni-bremen.de/sciamachy/mfactors/index.html>



CONCLUSIE



Delphine Faye (CNES)
VCCN symposium 2013

PRAKTIJK VOORBEELD EBL2

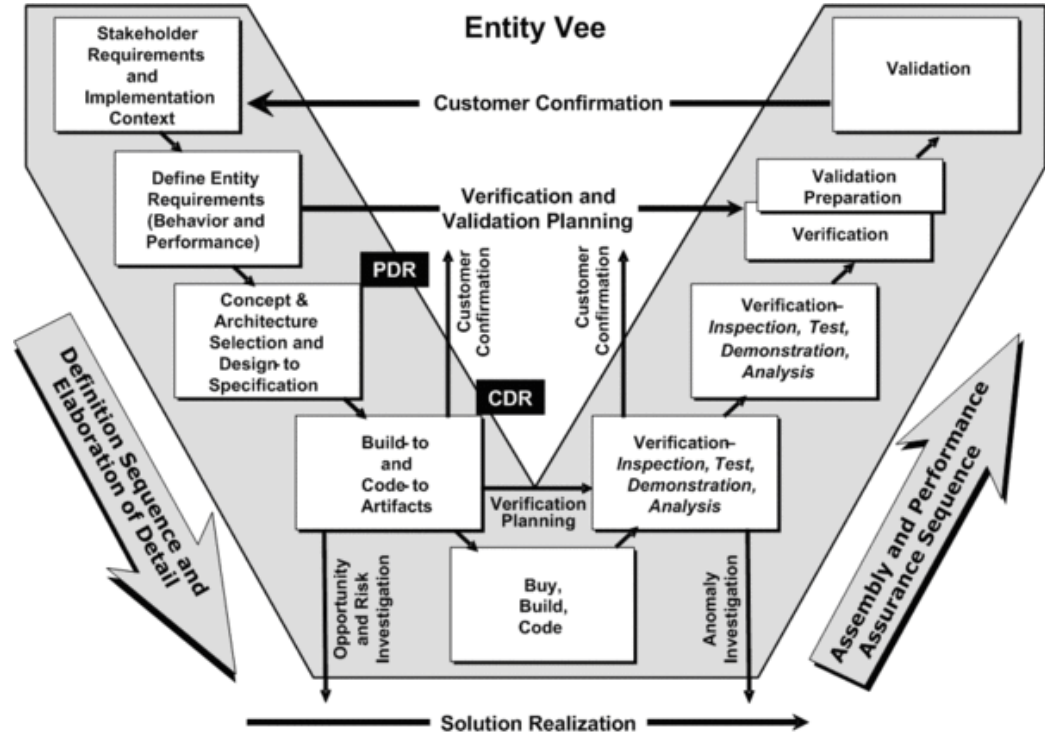
EBL2

- › EBL2 is een onderzoeksfaciliteit van TNO die gebruikt wordt voor het onderzoeken van levensduur van onderdelen die aan EUV blootgesteld worden
- › Ultra-schoon vacuüm
- › Verschillende gassen



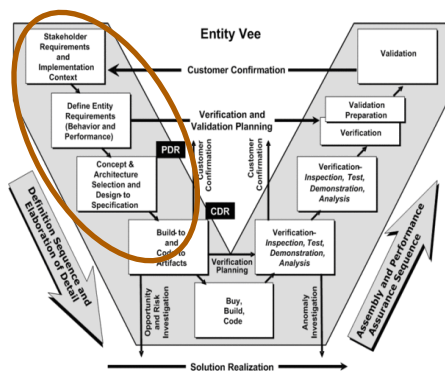
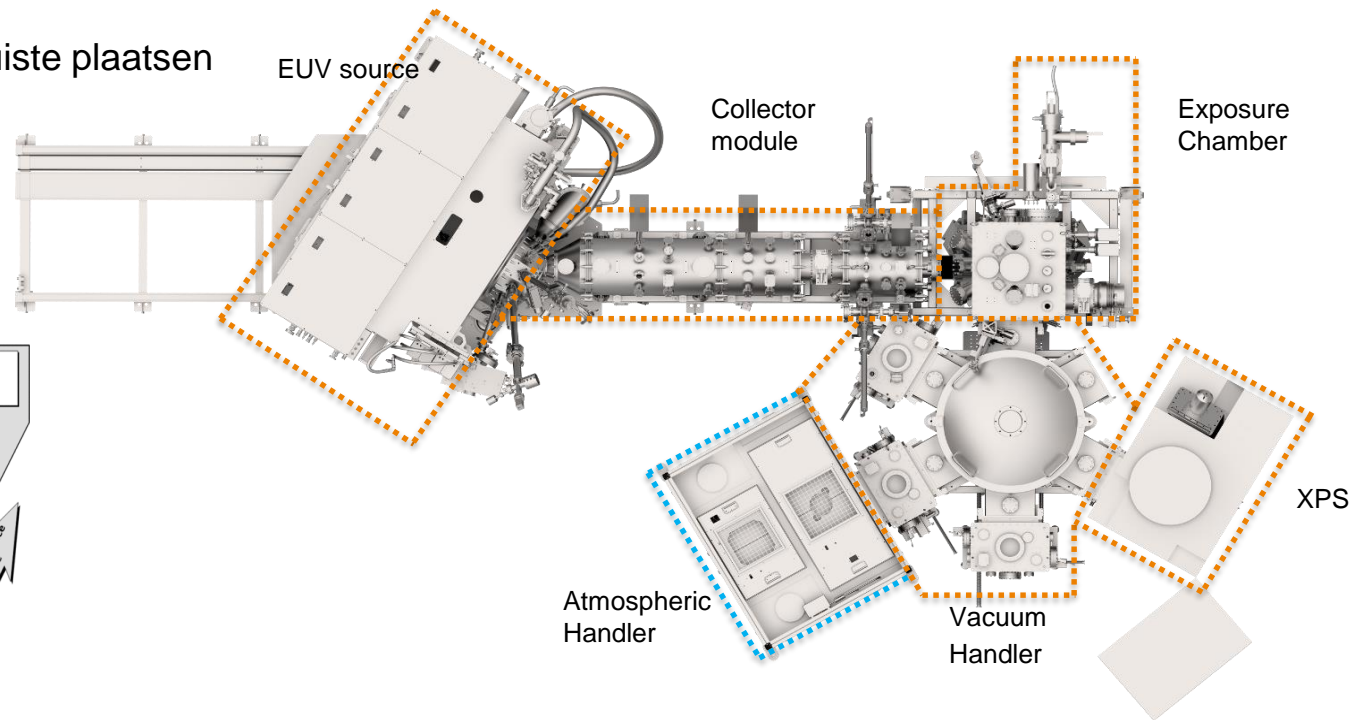
PRAKTIJK VOORBEELD ELB2

- › Systemaanpak
 - › vervuilingbudget

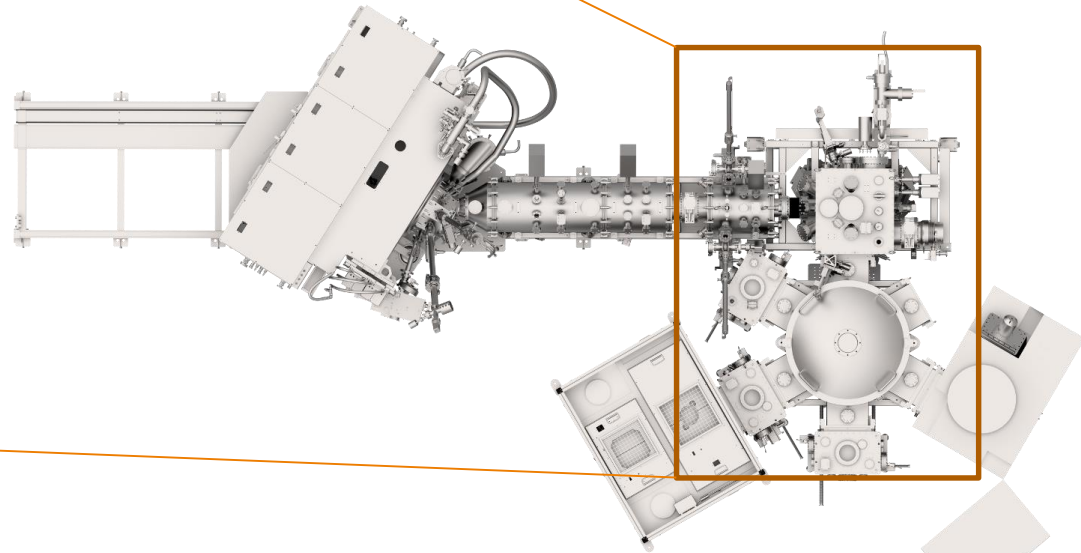
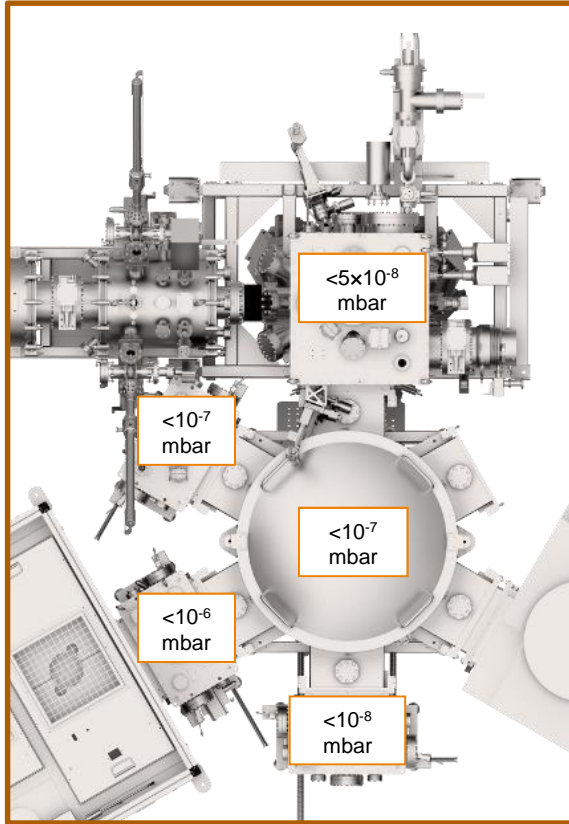


ONTWERP EBL2

› Extreem schoon op de juiste plaatsen

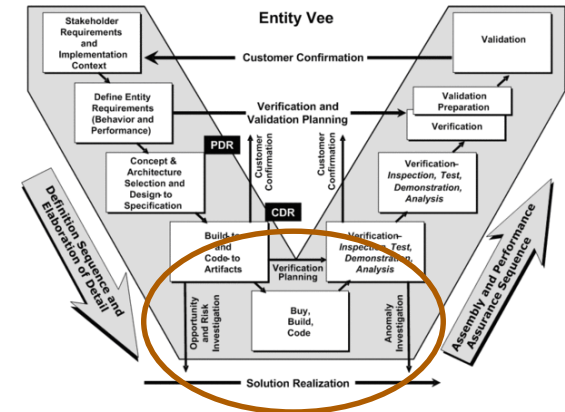


EBL2 VACUÛM



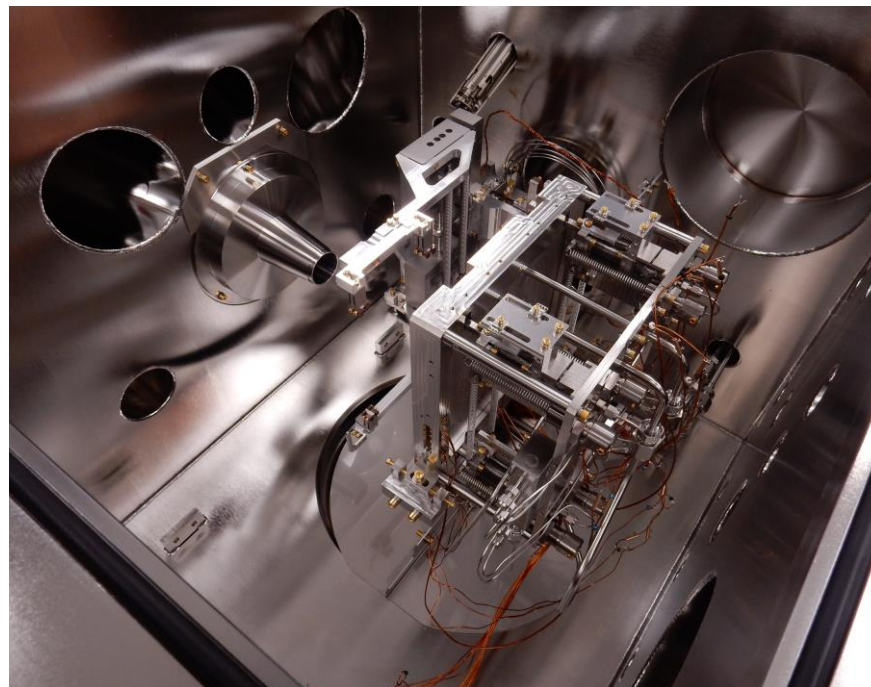
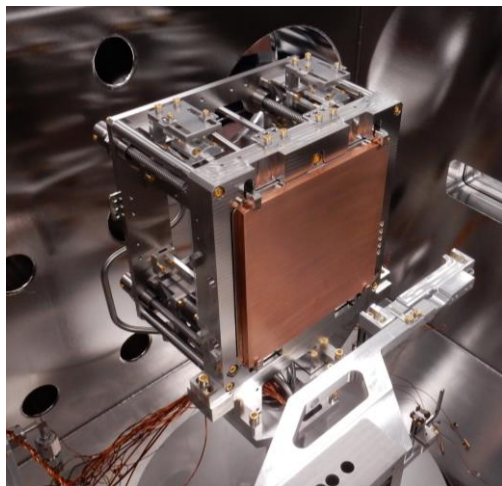
PRODUCTIE

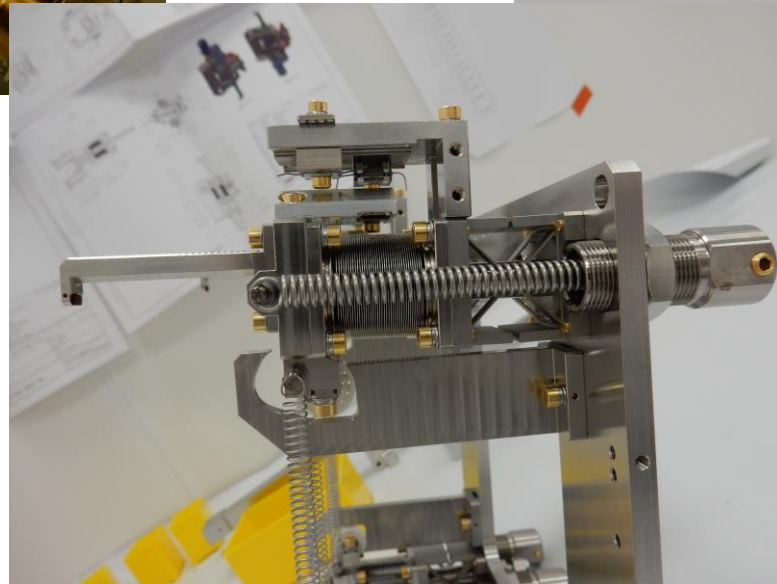
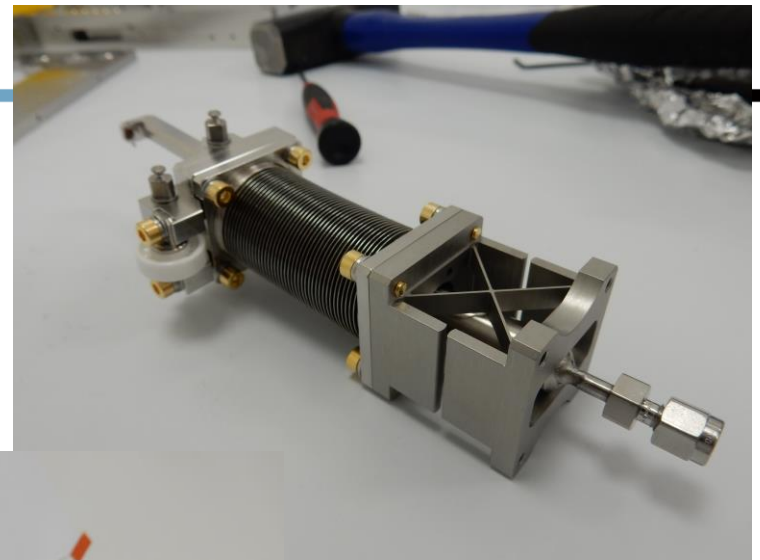
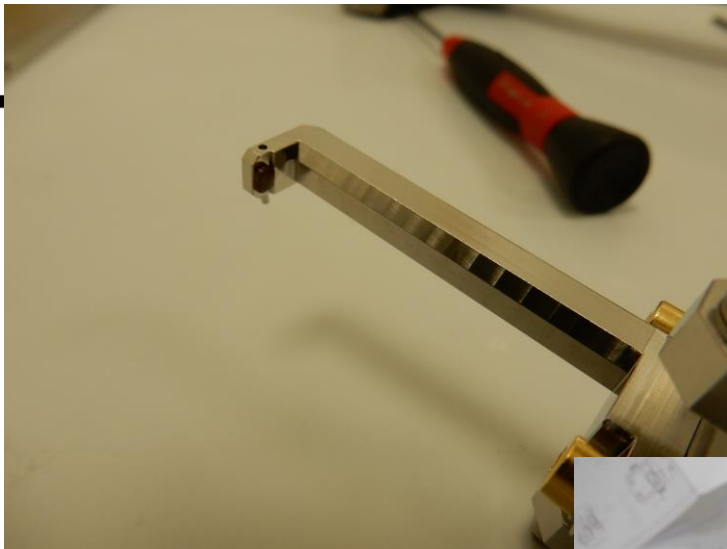
- › Materiaal en ontwerp moet reinigbaar zijn
 - › Bestendig tegen nat-chemisch reinigen
 - › Temperatuur bestendig
 - › Oppervlakken moeten bereikbaar zijn
- › Verspaningsmachines moeten schoon zijn
 - › Juiste koel- en smeermiddelen
 - › Geen tools gebruiken die in aanraking zijn geweest met materialen die niet toepasbaar zijn in vacuüm
- › Tijdens assemblage moet product schoon blijven
 - › Duidelijke instructie van personeel



PRODUCTIE / ONTWERP VOORBEELDEN

- › Sample handling in de exposurekamer
- › Strenge eisen op toegestane materialen
- › Onderdelen moeten reinigbaar zijn



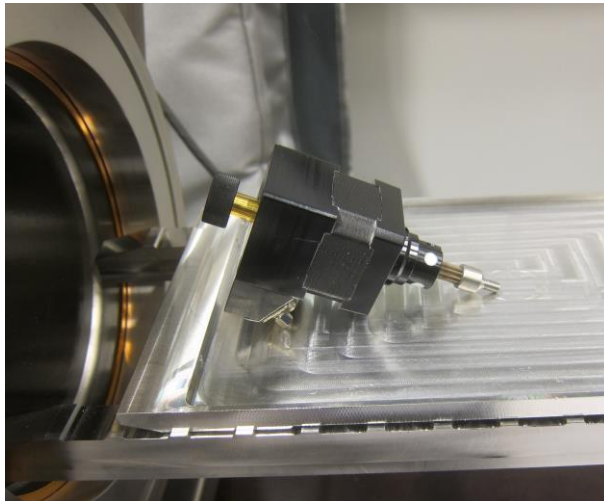
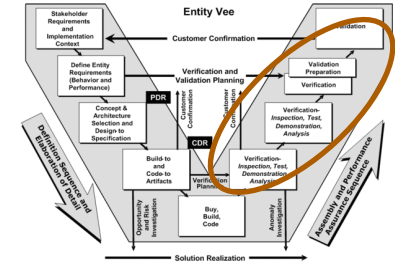




Chemische reinheid van producten

VALIDATIE UITGASSING

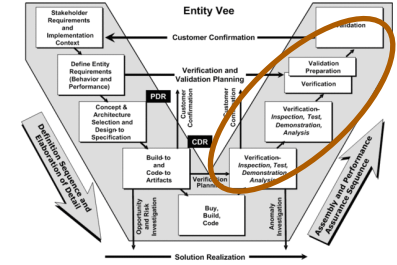
- › Geadsorbeerde moleculen komen vrij van een oppervlak
- › Welke massa en welke hoeveelheid kunnen we meten met een uitgasmetingopstelling
- › Vacuümopstelling met een RGA



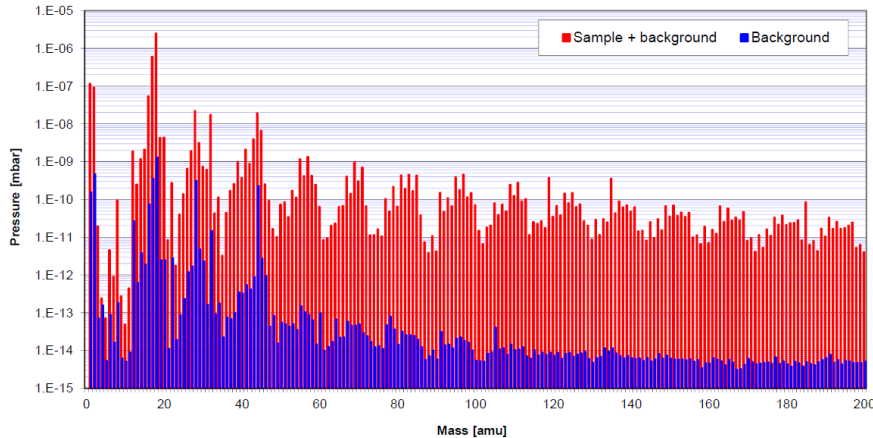
Chemische reinheid van producten



VALIDATIE UITGASSING



Mass spectrum after 10h pumping (pressure corrected)



Test details

Sample Id:		Pump speed [l.s^{-1}]:	25
Description:		System:	ATOM
Date:	20-Nov-15	Ratio: IG/RGA	0.6
Data filename:		RGA Id:	QMA 422: SN 44248116
Background file:		Ion gauge Id:	IG (YEA07221)
Filename:			
Operator:			Sample Outgassing 200amu v7
Comments:	Black coated stepper motor with sub-D connector, no vents to prevent for virtual leakage, no apparent (visible) lubrication outside		

Outgassing rate at 1h:

	Sample (background subtracted)	(background)
Q_{total} [mbar.l.s^{-1}]	NA	$7.50\text{E-}07$
$Q_{\text{H}_2\text{O}}$ [mbar.l.s^{-1}]	NA	$4.69\text{E-}07$
$Q_{\text{CxHy}<101\text{amu}}$ [mbar.l.s^{-1}]	NA	$6.41\text{E-}10$
$Q_{\text{CxHy}>100\text{amu}}$ [mbar.l.s^{-1}]	NA	$2.75\text{E-}11$
Q_{CxHy} [mbar.l.s^{-1}]	NA	$6.68\text{E-}10$
P _{ion gauge} [mbar]	NA	$3.00\text{E-}08$

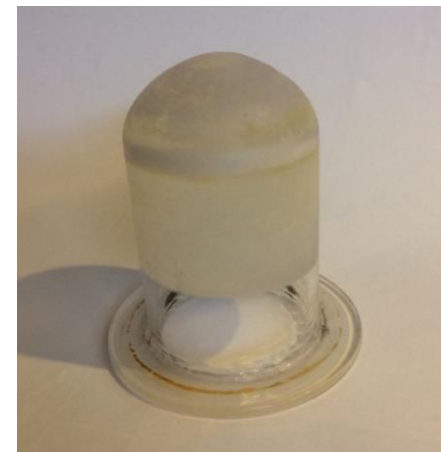
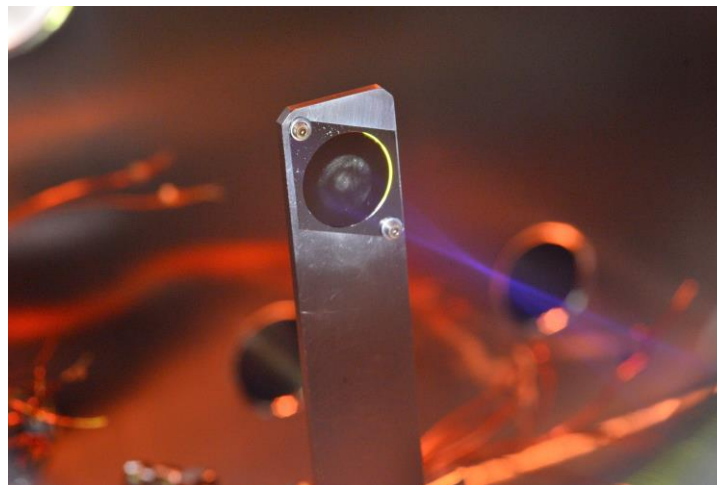
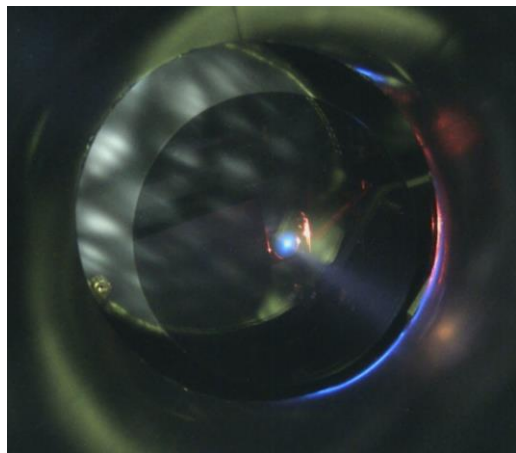
Outgassing rate at 10h:

	Sample (background subtracted)	(background)
Q_{total} [mbar.l.s^{-1}]	$8.79\text{E-}05$	$7.50\text{E-}08$
$Q_{\text{H}_2\text{O}}$ [mbar.l.s^{-1}]	$6.33\text{E-}05$	$3.30\text{E-}08$
$Q_{\text{CxHy}<101\text{amu}}$ [mbar.l.s^{-1}]	$4.51\text{E-}07$	$1.40\text{E-}10$
$Q_{\text{CxHy}>100\text{amu}}$ [mbar.l.s^{-1}]	$1.15\text{E-}07$	$1.72\text{E-}11$
Q_{CxHy} [mbar.l.s^{-1}]	$5.66\text{E-}07$	$1.57\text{E-}10$
P _{ion gauge} [mbar]	$3.52\text{E-}06$	$3.00\text{E-}09$

Comments: High outgassing of H₂O and CxHy, traces of CxHy/fluorocarbons (119, 135, 185 amu), high O₂ traces probably be due to virtual leakage

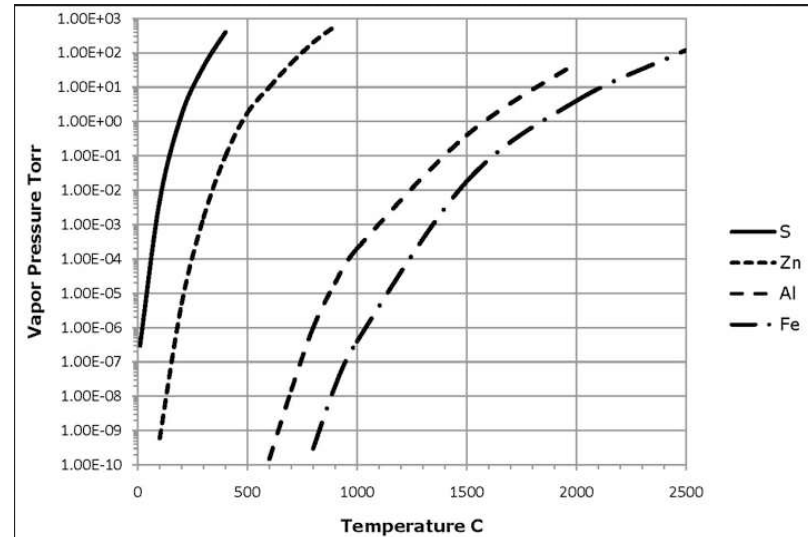
INTERACTIE VAN PROCESSEN MET BULKMATERIAAL

- › Vervuiling uit bulkmateriaal en
- › Vervuiling ten gevolgen van interactie met processen
 - › Oxideren en reducerende omgevingen



DAMPSPANNING VAN MATERIALEN

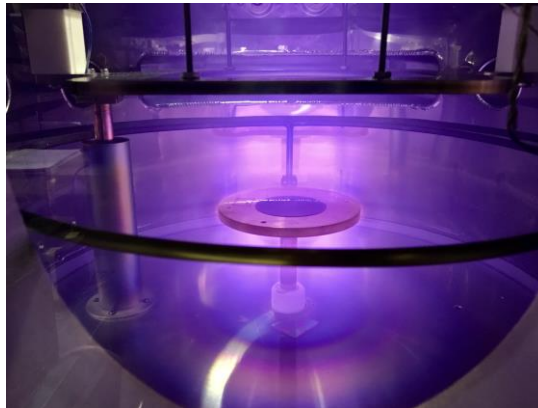
- › Sommige materialen zijn niet geschikt om in een hoog vacuüm toepassing gebruikt te worden, dit in verband met een te hoge dampspanning
- › Dampspanning van water is ~ 25 mbar



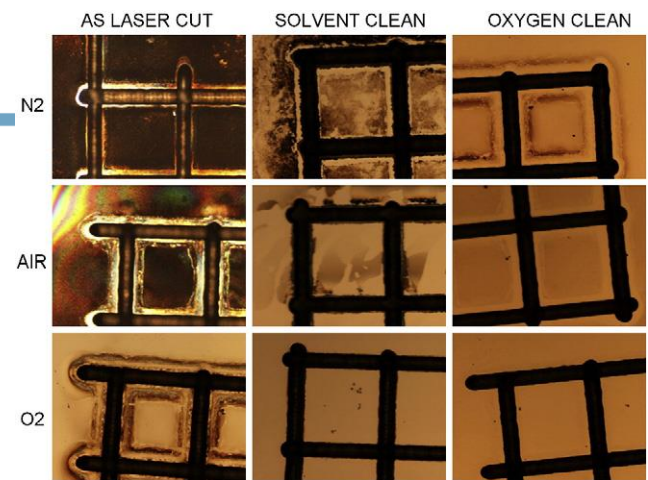
<https://www.mtm-inc.com>

OXIDERENDE OMGEVING

- › Atomair zuurstof in de ruimte
- › Etchprocessen die gebruikt worden in de semiconductor industrie



<http://sam.zeloox.xyz/category/plasma/>



Babic, Dubravko & Diduck, Quentin & Faili, Firooz & Wasserbauer, John & Lowe, Frank & Francis, Daniel & Ejeckam, Felix. (2011). Laser machining of GaN-on-diamond wafers. *Diamond and Related Materials*. 20. 675-681. 10.1016/j.diamond.2011.03.017.



NASA

REDUCERENDE OMGEVING

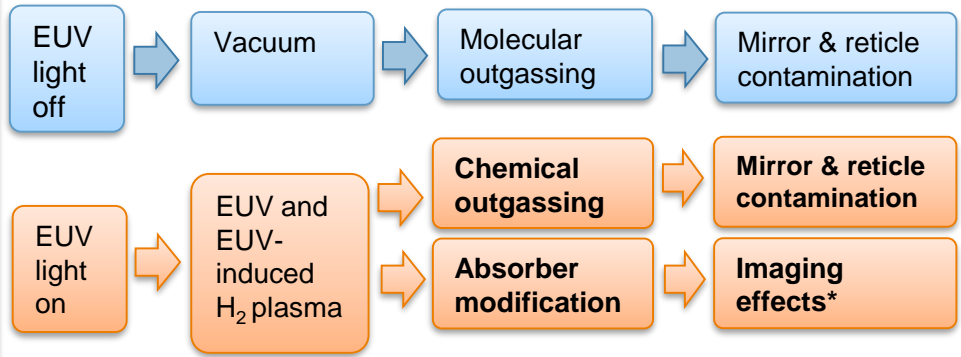
- › **Compatibility assessment of novel reticle absorber materials for use in EUV lithography systems**
 - › Jetske Stortelder, Arnold Storm, Veronique de Rooij, Chien-Ching Wu (TNO), Willem van Schaik (ASML) SPIE Advanced Lithography | February 27th , 2019

COMPATIBILITY TO EUV CONDITIONS

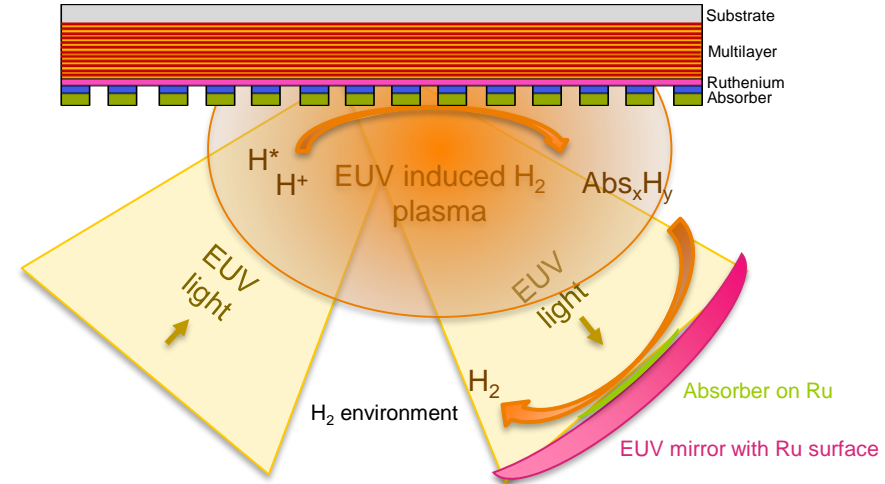
EUV reticle

EUV lithography system

Possible effects if absorber is not compatible



Schematic of EUV reticle with absorber stack exposed to EUV light in hydrogen environment leading to chemical outgassing (etching) and redeposition on a mirror

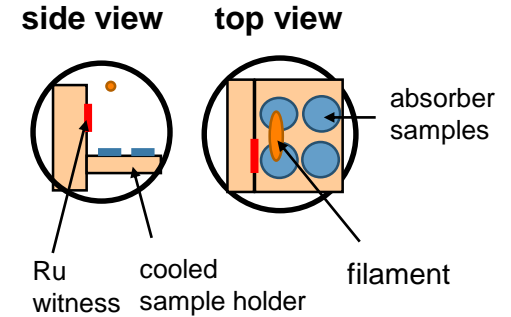
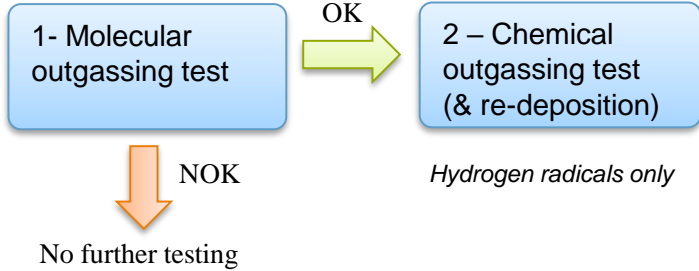


H* = hydrogen radicals
 H+ = various hydrogen ion species
 Abs_xH_y = volatile reaction product(s) of absorber and hydrogen

*Out of scope for assessment

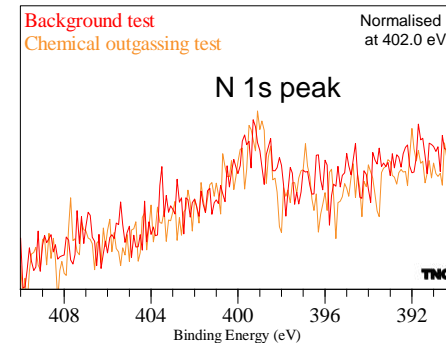
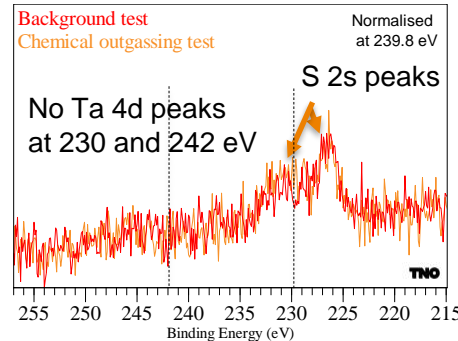
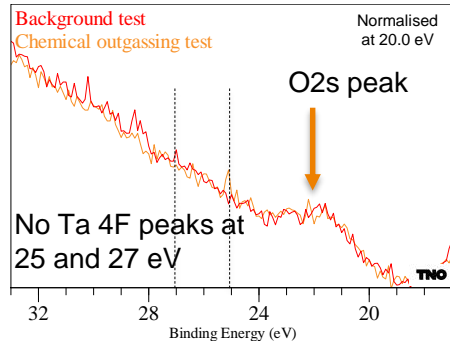
COMPATIBILITY ASSESSMENT

Stage 1 – Non EUV testing



Goal

Quantify absorber coated w



e size

5x55mm. er on Si te wafers.

The current GSA framework

Supplier's perspective

STEP 2 Clear overview of all requirements on TPD 160

1

Vacuum Cleanliness: Grade 1 requirements				
Requirement	Value	Verification	Reference	
H2O	3.23E-07 mbar.l/s	RGA	GSA Vacuum cleanliness Chapter 4	um cleanliness Chapter 4
CxHy nv	3.23E-09 mbar.l/s	RGA	GSA Vacuum cleanliness Chapter 4	um cleanliness Chapter 4
CxHy v	2.49E-10 mbar.l/s	RGA	GSA Vacuum cleanliness Chapter 4	um cleanliness Chapter 4
HIO elements Zn, Sn, Pb, In	<0.1 at%	XPS	GSA Vacuum cleanliness Chapter 5	um cleanliness Chapter 5
HIO elements Mn	<0.2 at%	XPS	GSA Vacuum cleanliness Chapter 5	
HIO elements F, Cl	<0.3 at%	XPS	GSA Vacuum cleanliness Chapter 5	
HIO elements S, P, Si, Na, Ca, HIO elements N	<0.5 at%	XPS	GSA Vacuum cleanliness Chapter 5	
Manufacturing process	<1 at%	XPS	GSA Vacuum cleanliness Chapter 5	
Requirement		Release certificate	GSA WOW for cleanliness	
Requirement				
Particles	VC grade 1			
Particles	0	UV-A	GSA Surface Cleanliness Chapter 6	
Particles	0	BL	GSA Surface Cleanliness Chapter 7	
Stains	0	UV-A	GSA Surface Cleanliness Chapter 7	
Particles concentration	≤SCP Class 6 (0.5 μm)	PMC+SEM/EDX	GSA Surface Cleanliness Chapter 8	
Particles concentration	≤SCP Class 4 (10 μm)	PMC+PartSens	GSA Surface Cleanliness Chapter 8	
PMC sample location(s) + accompanying correction factor	Figure 1		GSA Surface Cleanliness Chapter 8	
PMC sample time	After cleaning		GSA Surface Cleanliness Chapter 8	
Manufacturing process	SC Grade 1	Approved for release	GSA Surface Cleanliness Chapter 9	

l when to put

typical lower detection limits (LDL) → no spec on TPD

TPD60 shall state that vacuum cleanliness w.r.t. outgassing must be secured by a proven & frozen process.



Chemische reinheid van producten

EBL2 VOORBEELDEN

› Enclosure



CONCLUSIE

- › In de toekomst zal er om steeds schonere producten gevraagd worden
- › Het is van groot belang om samen te werken om haalbare eisen op te stellen tegen reële kosten
- › Dit begint met elkaar te begrijpen, met wat we nu van elkaar eisen → deze werkgroep

› **BEDANKT VOOR UW AANDACHT**

Voor meer inspiratie:
TNO.NL/TNO-INSIGHTS

TNO innovation
for life

XPS (OPTIE)

- › X-ray Photo-electron Spectroscopy (XPS) is een methode om te meten wat in de top 10 nm van een materiaal zit
- › Sample omdat volledige producten niet in de XPS passen
- › Sample dat gemeten wordt moet het volledige proces doorlopen hebben;
 - › Hetzelfde materiaal
 - › Dezelfde mechanische bewerking
 - › Dezelfde nat-chemische reiniging
 - › Dezelfde opslag

