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**Innovative and environmental friendly Fluorine F₂
based cleaning process to replace C₂F₆, CF₄ and NF₃
as cleaning gas**

**SPCC Conference
Santa Clara, April 19th 2016**



**Solvay Special Chem
Marcello Riva**

Outline

- Intro – PECVD cleaning technology
- Drivers for F₂-based chamber cleaning
- Facilitation example for F₂-gas
- Hardware and experimental
- Cleaning results F₂/Ar/N₂
- 500 wafer run
- Waste gas data
- Summary and conclusions

PECVD Chamber Cleaning

- Currently used cleaning gases:

Oxide / nitride films (PECVD): NF_3 , CF_4 , C_2F_6 , C_3F_8

Poly-Si CVD, MOCVD of W and TiN: NF_3

- CVD chambers need frequent cleaning of all process-relevant reactor surfaces to sustain particle- and defect free film deposition

Drivers for F₂-based Plasma-Cleaning

- Proposed gases: Low GWP* Gas Mixtures
- F₂ (GWP=0) as NF₃, PFCs (perfluorocarbon) alternative

	GWP	Life time			GWP	Life time
CF ₄	7390	5000		NF ₃	17200	740
CHF ₃	11700	264		SF ₆	22800	3200
CH ₂ F ₂	650	5,6		c-C ₄ F ₈	8700	3200
C ₂ F ₆	12200	10000		C ₄ F ₆	~0	~0
C ₃ F ₈	7000	2600		c-C ₅ F ₈	90	~1

*GWP (Global Warming Potential); CO₂ = reference = 1

Properties of F₂-based cleaning gas mixture

- F₂ diluted in N₂ and Ar (compressed gas)
- Transportable in standard gas cylinder
- Corrosive, **not inflammable, not explosive**
- A diluted F₂-gas mixture is best for an efficient chamber clean
- F₂ mixtures require a passivation of an existing stainless steel gas delivery system (one time procedure)

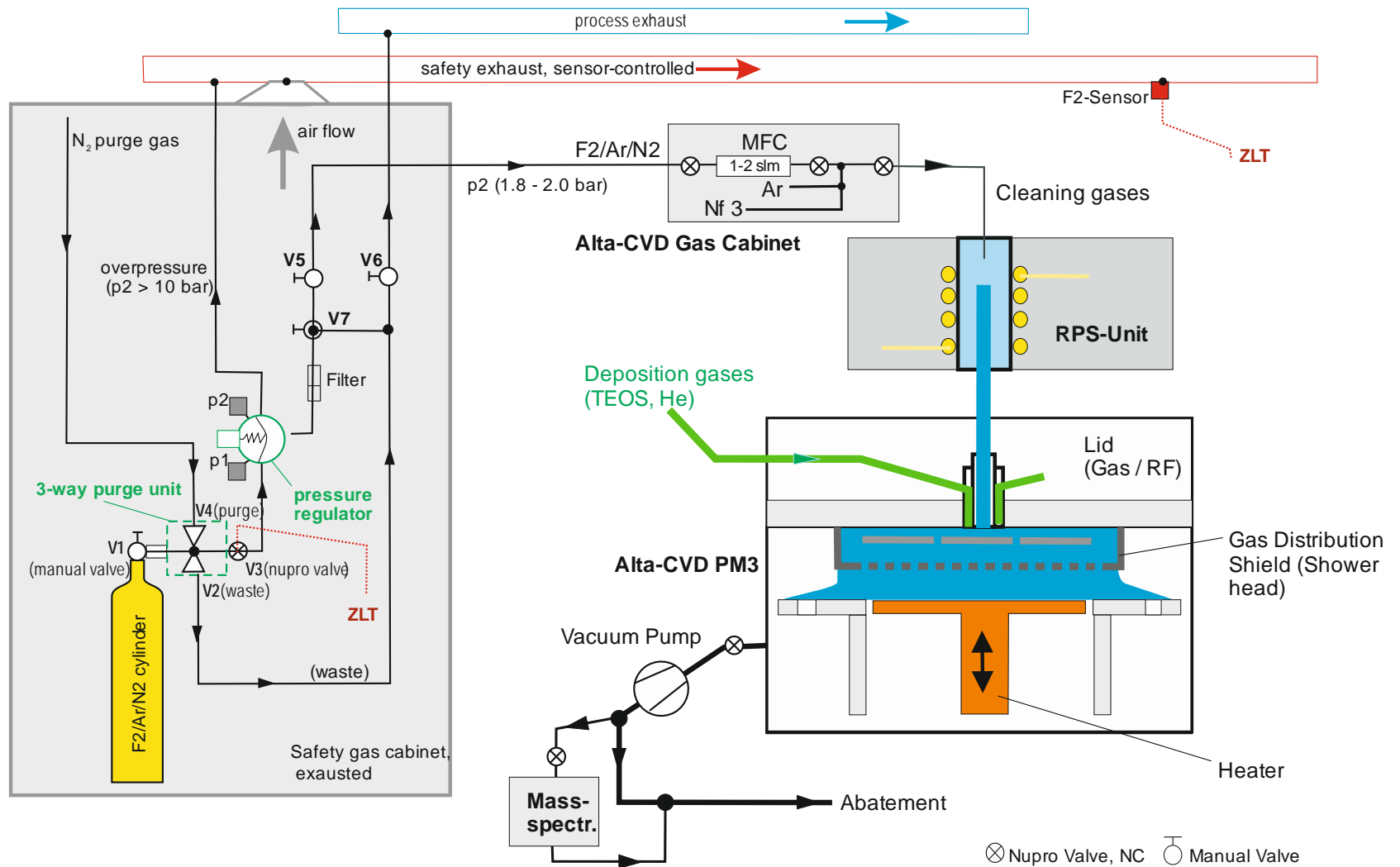
F₂ Gas Mixture – Gas Cabinet Example

- Gas mixture 1: F₂/Ar/N₂ → 13,56 MHz plasma
- Gas mixture 2: F₂/Ar/N₂ → 400 kHz RPS-unit
- Safety gas cabinet
- 3 way valve, purge gas N₂
- Gas cylinder: 10L, 100 bar

F₂/Ar/N₂ cylinder



F₂/Ar/N₂ Gas Mixture – Facilitation Example

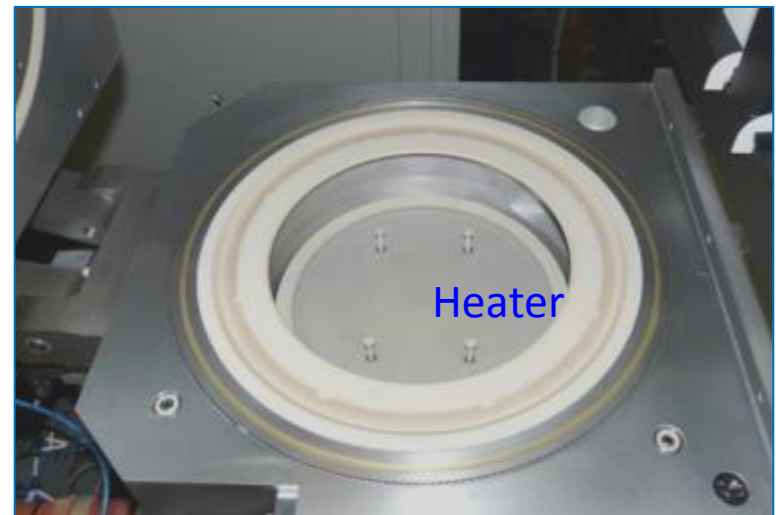
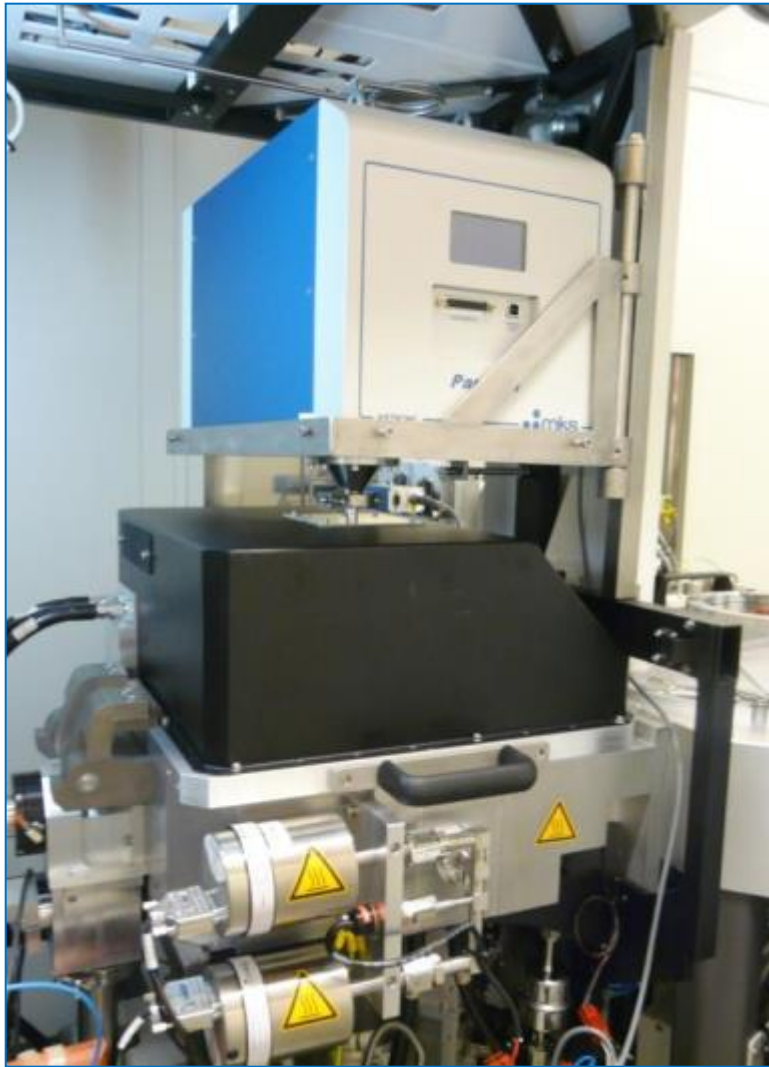


CVD Tools at Fraunhofer EMFT (200mm)

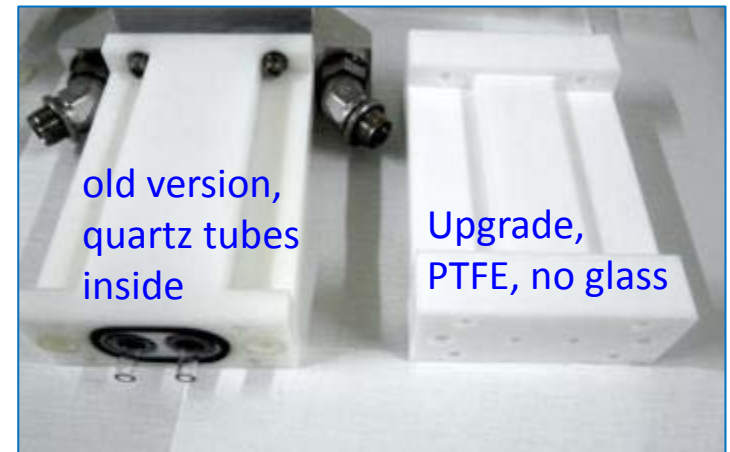
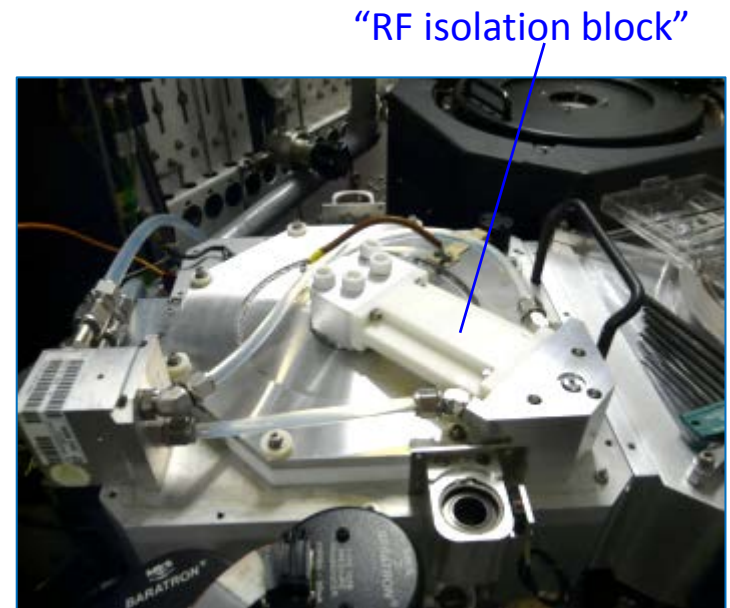
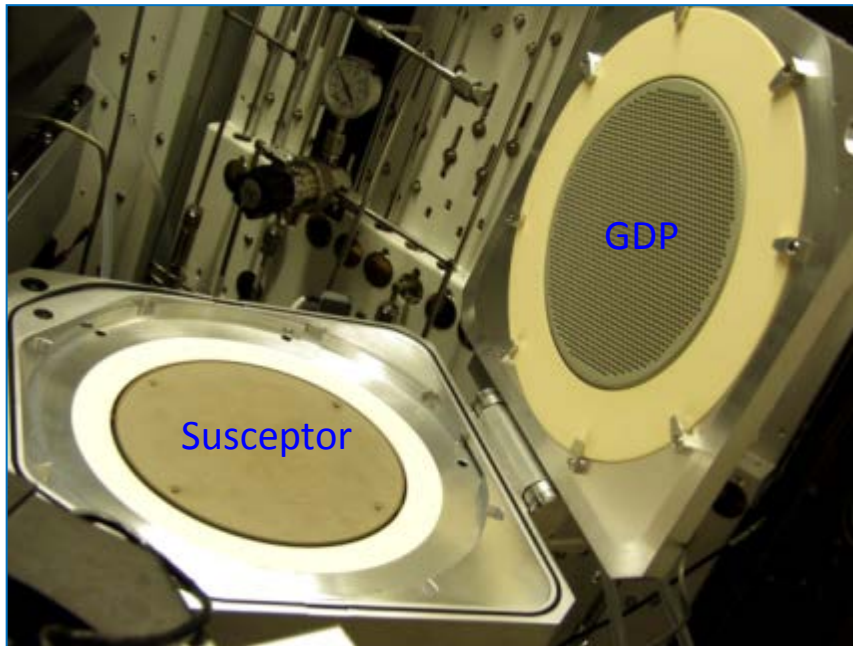
- Alta-CVD , Brooks VX400
PECVD for SiO₂ films - PETEOS, BPSG
 - 13,56 MHz plasma clean, C₂F₆ / NF₃ based
 - RPS (remote plasma source) clean, NF₃ based
- AMAT PECVD, P 5000
PECVD for SiO₂ films, lamp-heated
 - 13,56 MHz plasma clean, C₂F₆/NF₃ or CF₄ based



RPS Unit on Top of Alta-CVD Chamber



AMAT P5000 PECVD - Details



Commercially available upgrade

SiO₂ Cleaning Rate – Experimental

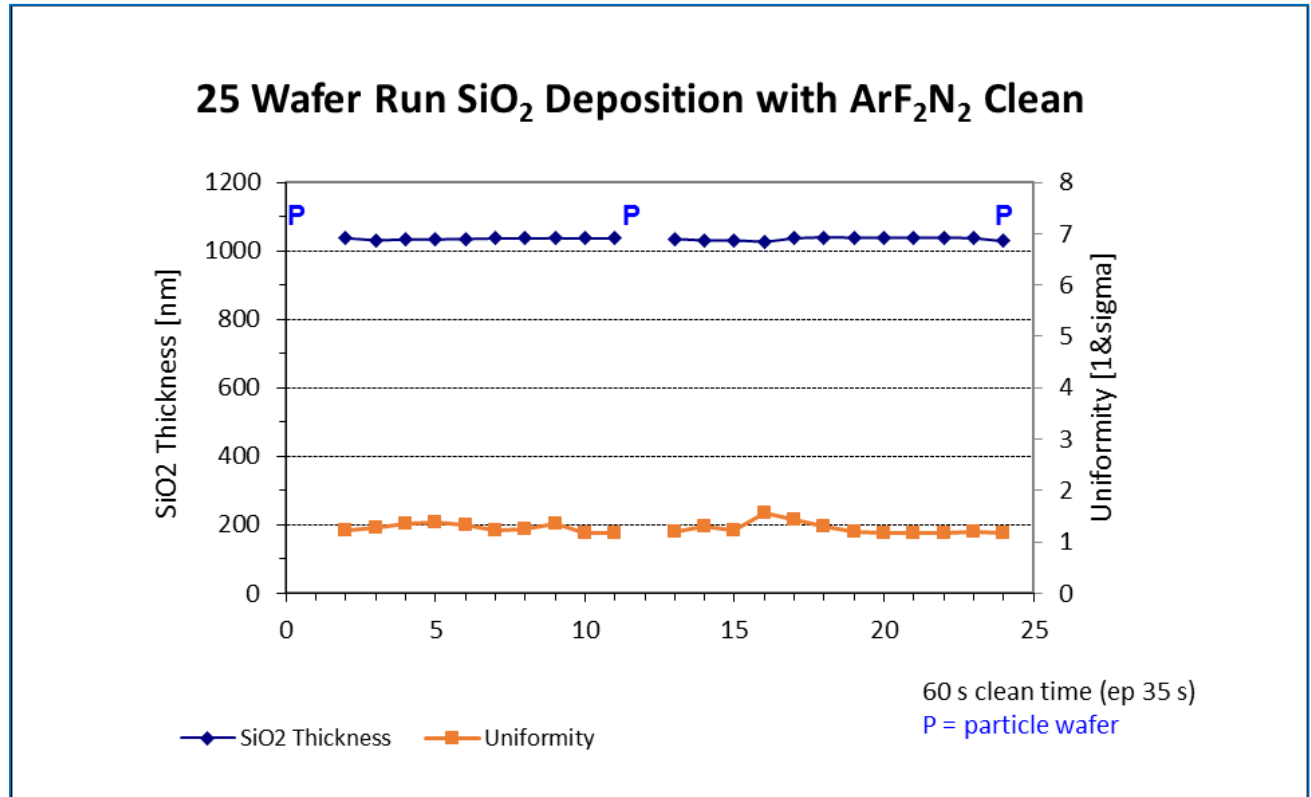
- Deposition of 2 μm PETEOS-film, 200mm Si-substrates
- Thickness measured with reflectometer / ellipsometer
- SiO₂-Etch rate calculated from post-etch TEOS film thickness
- Constant parameters:
55 deg. C wall / lid temp., 400 deg. C heater temperature
- Parameter Variations:
Gas flows, chamber pressure, RF-power, Spacing
- 30% higher SiO₂ cleaning rate compared to C₂F₆

13,56 MHz Plasma Cleaning Process (2)

- Repeatability of SiO₂ deposition, 3 x 25 wafer

Run #	# of adders (particle size $\geq 0,25\mu\text{m}$)			
	Slot 1	Slot 12	Slot 25	Average
1	38	7	21	22
2	5	5	32	14
3	11	2	6	6
Mean	18	5	20	14

AMAT P5000
lamp-heated
CVD, 200mm



13,56 MHz Plasma Cleaning Process (4)

Amount of cleaning gas needed for 25 Wafer Lot (1µm SiO2 depo / wafer):

C2F6/O2:	tot. flow/wafer [slm]	tot. flow /lot [slm]	tot. gas/lot [g]	F2/lot [g]
C2F6-Flow	0,9	21,6	132,7	114,4
O2-Flow	0,9	22,2	31,7	
NF3-Flow	0,1	1,9	5,9	
Mean SiO2-rate ~1100nm/min				
CF4/O2:	tot. flow/wafer [slm]	tot. flow /lot [slm]	tot. gas/lot [g]	F2/lot [g]
CF4-Flow	0,8	19,3	75,7	65,3
N2O-Flow	0,3	7,0	18,8	
Mean SiO2-rate ~1200nm/min				
F2/Ar/N2:	tot. flow/wafer [slm]	tot. flow /lot [slm]	tot. gas/lot [g]	F2/lot [g]
F2/Ar/N2-Flow	0,8	19,5	27,1	6,6
Mean SiO2-rate ~1500nm/min				
Ratio C2F6 : F2	17 : 1			
Ratio CF4 : F2	10 : 1			

13,56 MHz Plasma Cleaning Process (5)

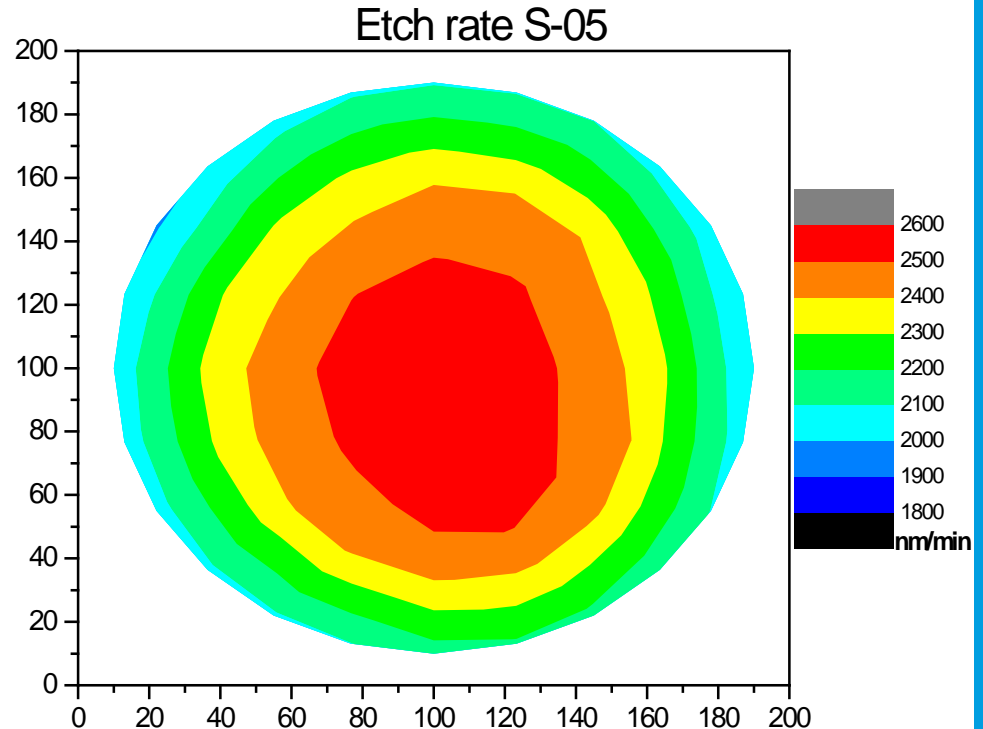
Bond Dissociation energies			
Molecule			Diss. Energy [kJ/mol @ 298K]
N ₂	-->	N + N	945
F ₂	-->	F + F	155
NF ₃	-->	NF ₂ + F	243
NF ₂	-->	NF + F	318
NF	-->	N + F	301
NF ₃	-->	N + F + F + F	862
CF ₄	-->	CF ₃ + F	506
C ₂	-->	C + C	607
O ₂	-->	O + O	498
N ₂ O	-->	NO + N	115
source: united states department of commerce, national bureau of standards, Lewis M. Branscomb			

400 kHz RPS Cleaning Process

- Gas mixture 2
- Monitored: SiO₂-deposition rate, particles in SiO₂-film25-wafer runs in auto-mode
- 500 wafers deposited, clean after every wafer
- Optical inspection of process kit parts
- F₂ gas mixture has identical cleaning rates of SiO₂ ≥ 1,0 μm/min compared to a BKM NF₃-based recipe
- Drop-In recipe to substitute Ar/NF₃ chemistry (same pressure, total flow, spacing, step times)
- Potential for optimization still given
- Cleaning efficiency of F₂ gas mixture ≥ factor 1,2 compared to NF₃

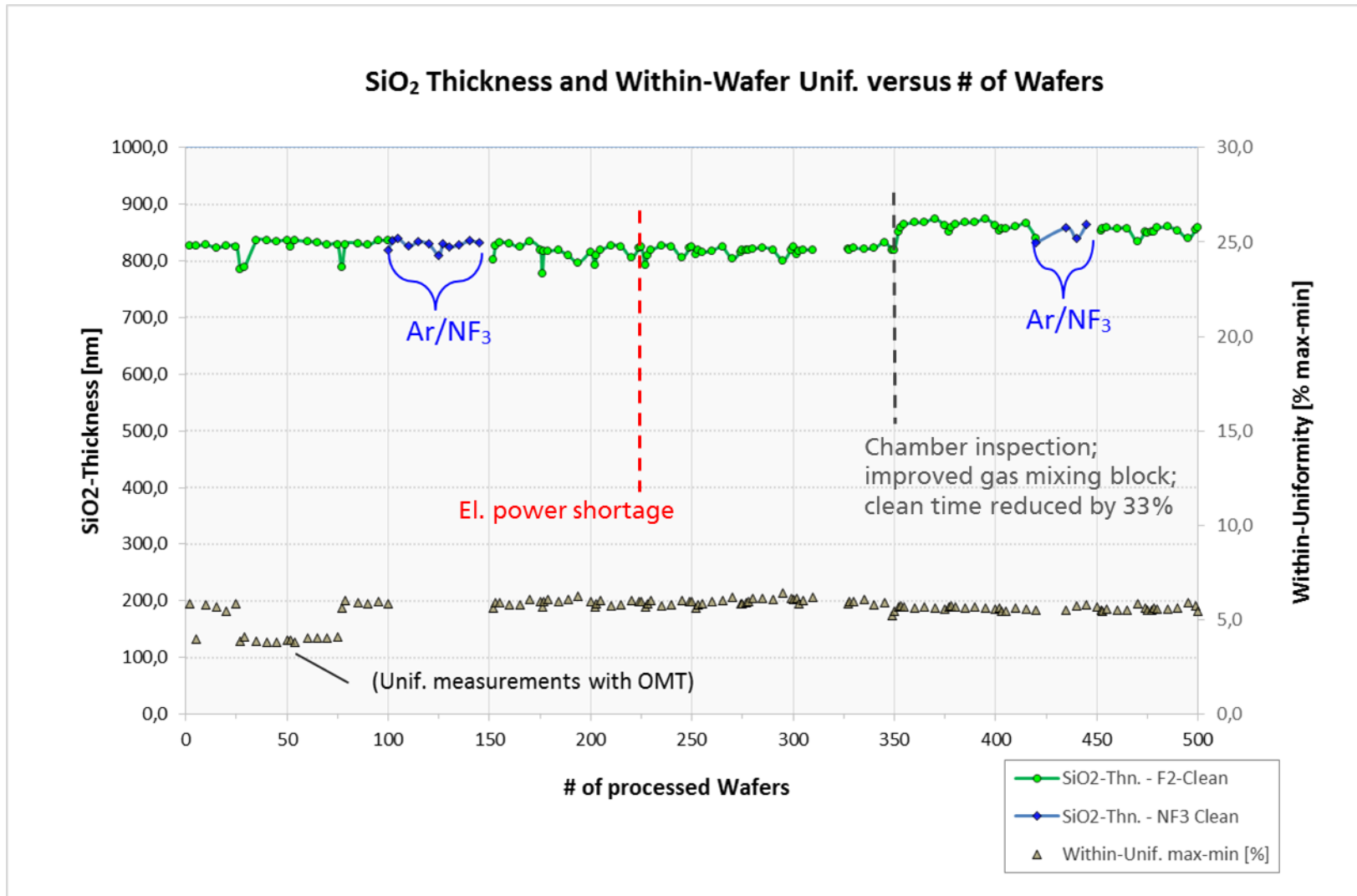
400 kHz RPS Cleaning Process (2)

- 4 Step process:
 - Ar-Flow and Ignition
 - F₂-addition to Ar
 - Inner clean
 - Outer clean
- Etch behavior: Center fast



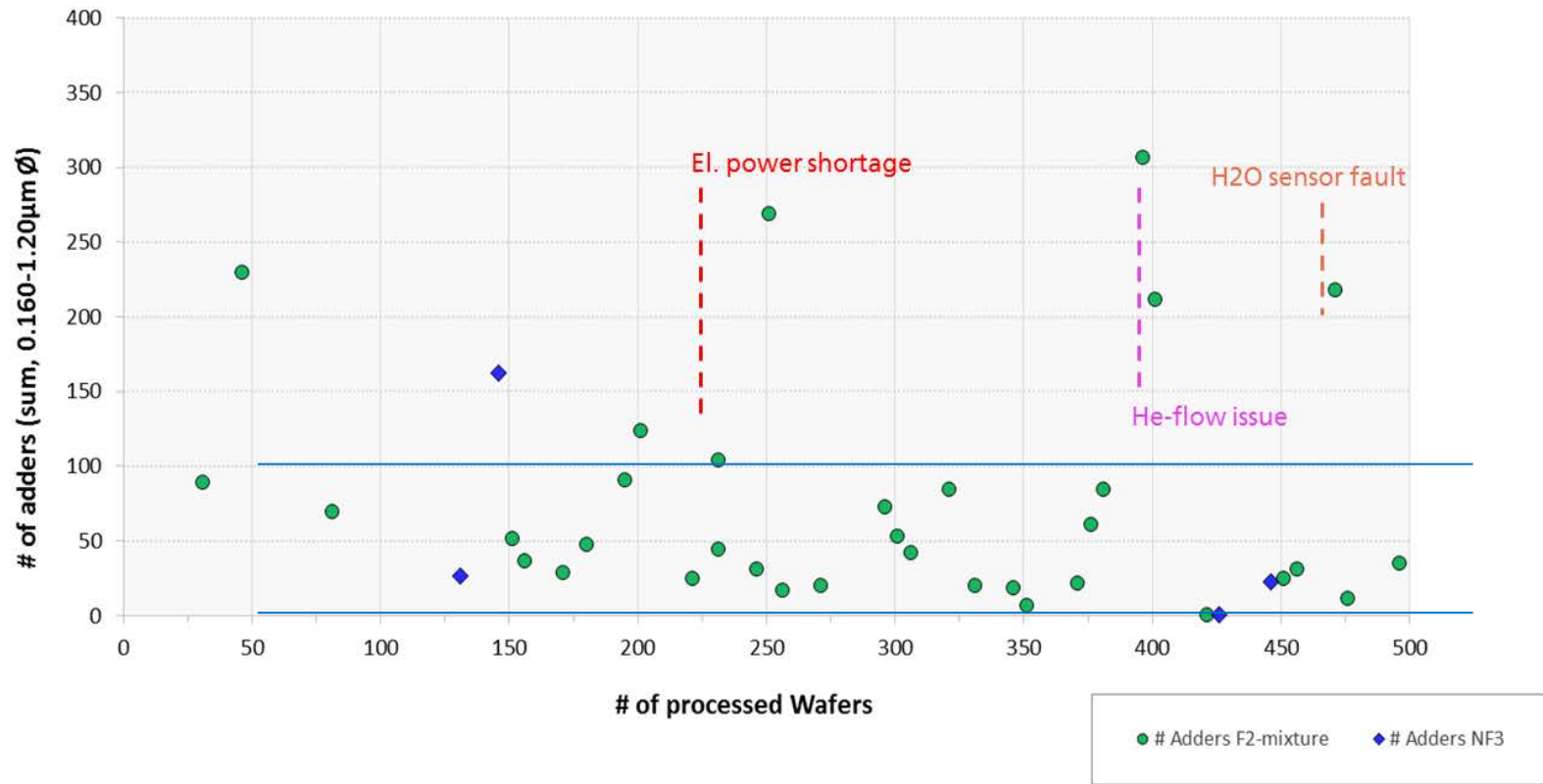
SiO₂-etch rate of complete NF₃-cleaning recipe with RPS-Unit

400 kHz RPS – 500 Wafer Run - Results (2)



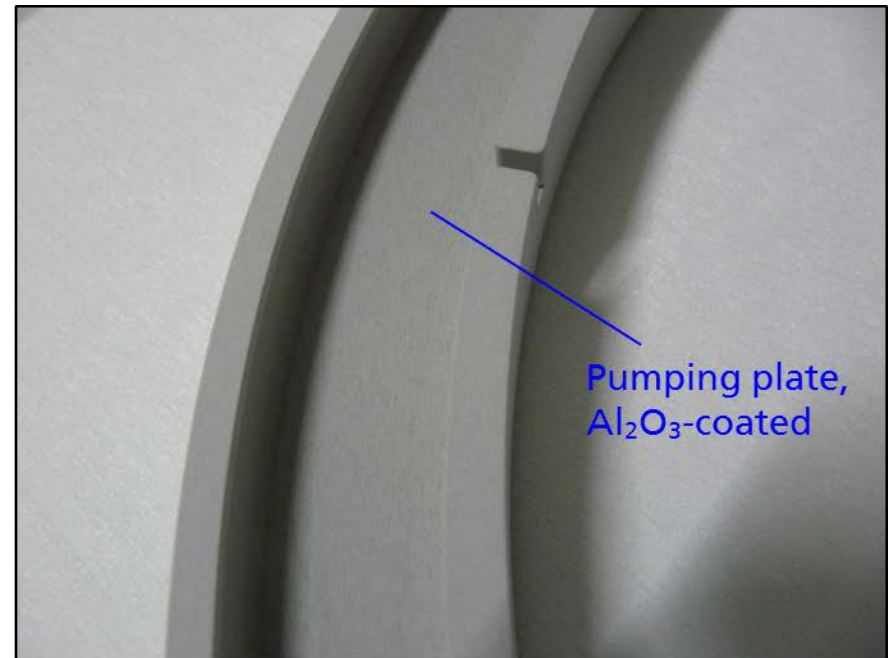
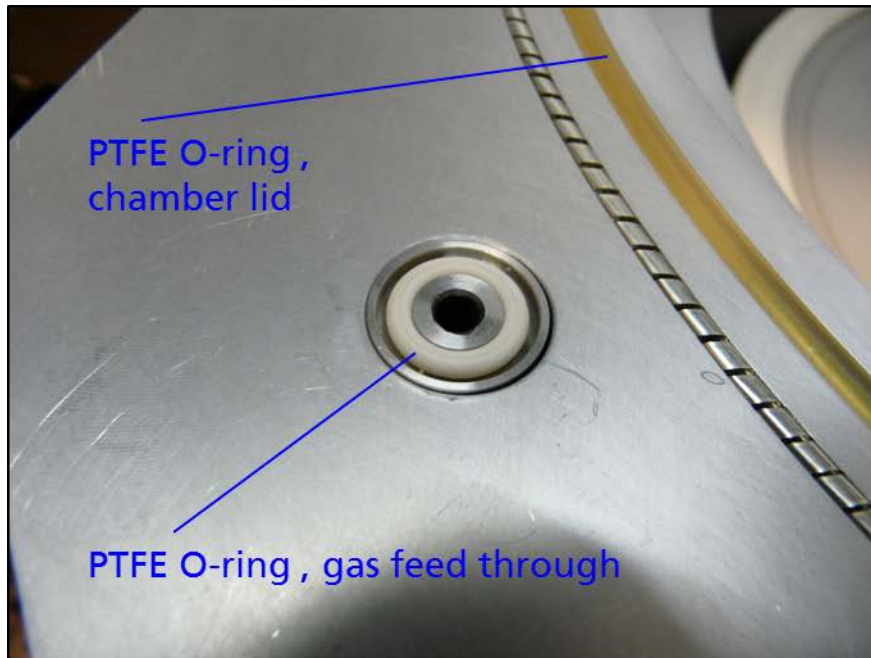
400 kHz RPS – 500 Wafer Run - Results (3)

Particle counts versus # of processed wafers

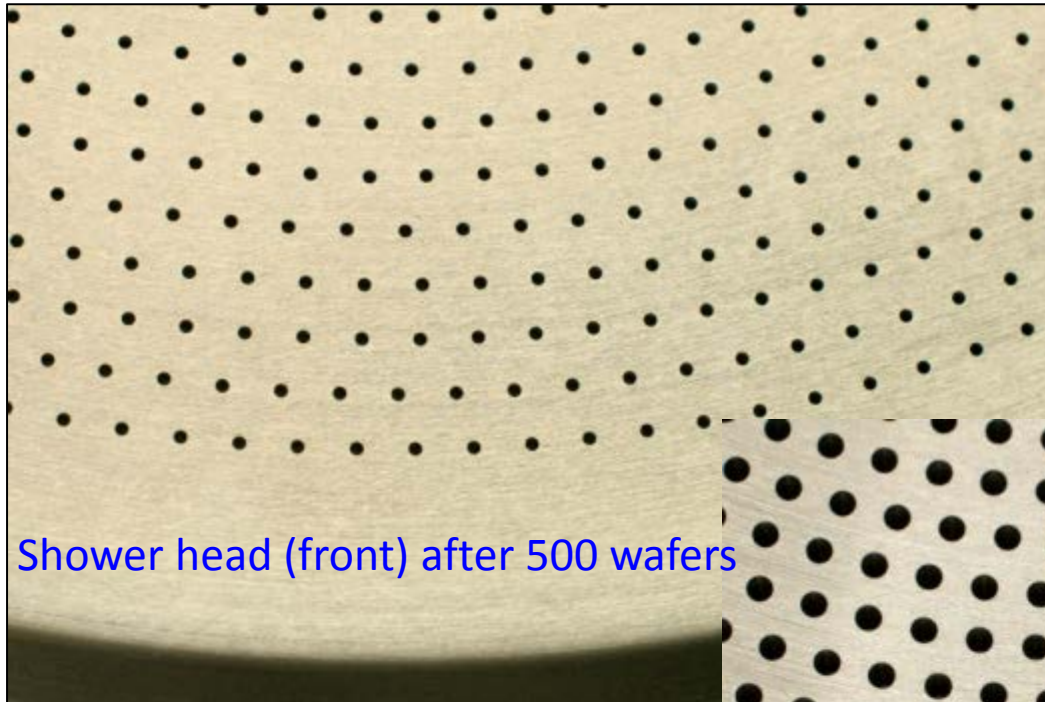


400 kHz RPS – 500 Wafer Run - Results (5)

- Optical inspection showed no noticeable effects of the cleaning plasma on process kit parts
- PTFE O-rings fully intact, no signs of wear after 500 processed wafers



400 kHz RPS – 500 Wafer Run - Results (6)



Shower head (front) after 500 wafers

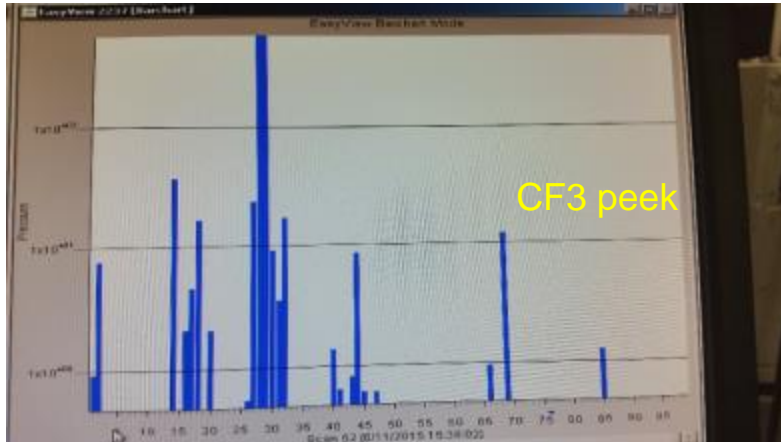


Shower head (backside) after 500 wafers

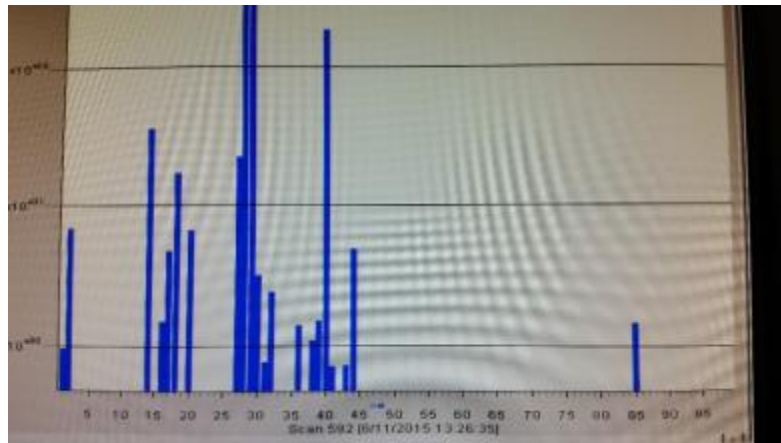
Waste Gas Analysis

- Atmospheric mass spectrometer was mounted behind process pump exhaust
- In case of C_2F_6 compared to F_2 -mixture, the absence of the big CF_3 peak confirms our early estimation of a cleaning efficiency factor >17 for F_2 -mixture compared to C_2F_6

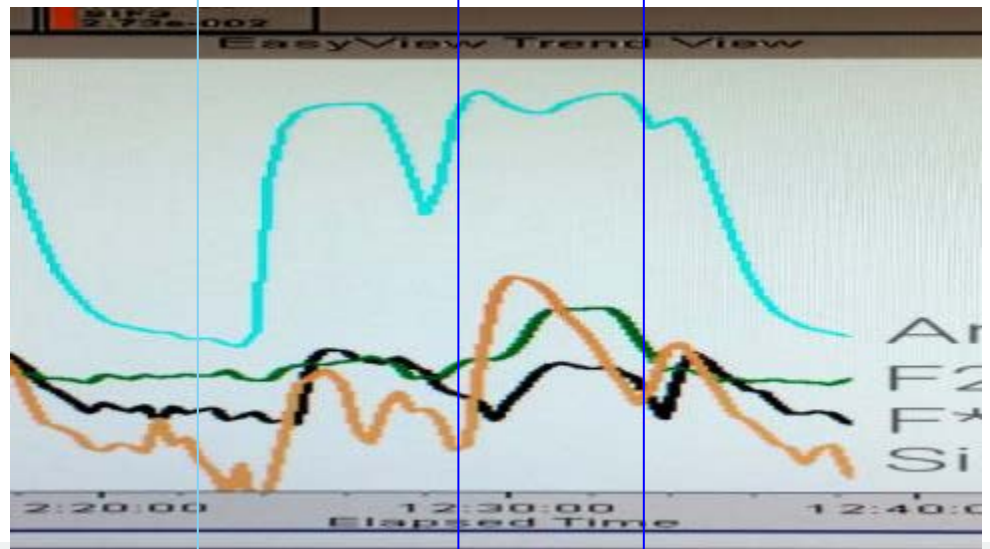
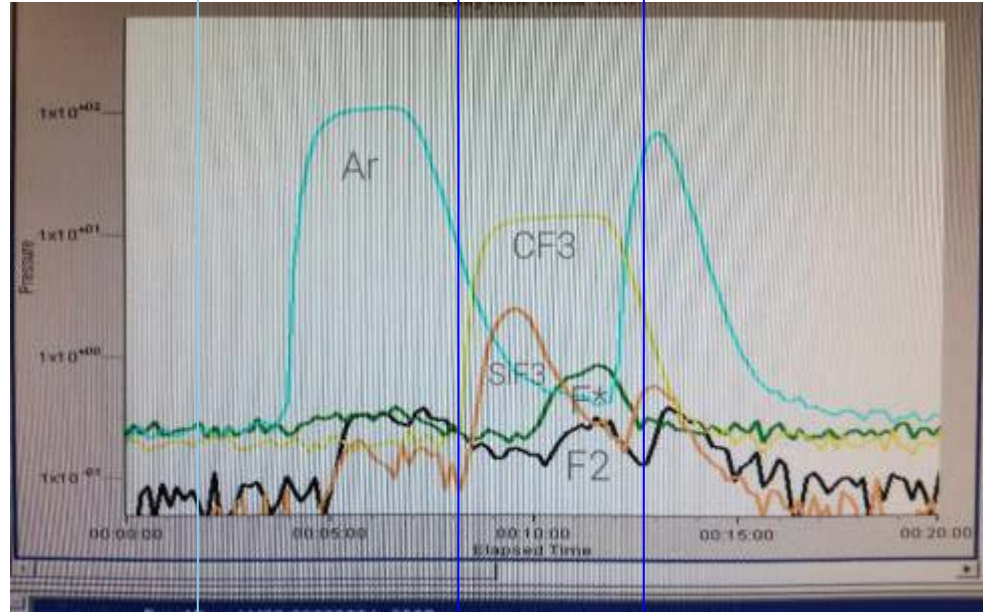
Waste Gas Analysis (2)



C₂F₆ Clean, 13,56 MHz parallel-plate



F₂ - gas mixture 2, 440kHz RPS



Summary and Conclusions

- Higher cleaning efficiency for F_2 gas mixtures
- F_2 gas mixtures showed similar performance for particle density and process kit degradation compared to NF_3 / PFCs
- Extended life time of process kit parts expected, especially for processes using PFCs as cleaning gases (no CF_3 radicals)
- Environmental-friendly processing
- Drop-in processes for NF_3 , C_2F_6 and CF_4

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