SOLVAY

Fluorine :
Optimised and sustainable cleaning agent for CVD processes

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Plasma Etch Users Group Meeting
15th May, 2008.

Confidentiality Statement

Outline

Industry driving forces

Potential benefits of F_2

Cleaning for LPCVD

Cleaning for PECVD

Discussion of results / next steps

Summary

Industry Driving Forces

ITRS ESH 2007 extracts

ESH Difficult Challenges

Need to develop equipment and processes that meet technology demands while reducing impact on human health, safety and the environment, both through the use of more benign materials, and by reducing chemical quantity requirements through more efficient and cost-effective process management

Need to reduce emissions from processes using high GWP chemicals

Need to reduce total CO_2 *equivalent emissions*

Industry Driving Forces
ITRS ESH 2007 extracts

Technical Thrust ESH Technology Requirements – Interconnect

PFCs are used extensively in interconnect dry etch and chamber cleaning applications. A potential new source of substantial PFC emissions is 3D interconnect where PFC such as SF_6 *are being considered for through-silicon via etch.... In recent years, chamber clean processes that do not emit high global warming potential by-products have been successfully developed. This concept should be carried over to etch.*

With increased focus on energy conservation, the power requirements of plasma enhanced CVD and etch equipment must be minimised.

Technical Thrust ESH Technology Requirements – Front End

Continued use of PFCs in front end plasma etch as well as chamber cleans will necessitate near term optimisation / increased gas utilisation. Over the longer term, alternative chemistries for PFCs that do not emit PFCs as by-products need to be developed.

Industry Driving Forces

ITRS ESH 2007 – Chemical Restrictions Table

ESH Intrinsic Requirements

- The risk assessment should include a check of the chemical against the Chemical Restrictions Table, to ensure the chemical is not banned or under some regulatory watch.

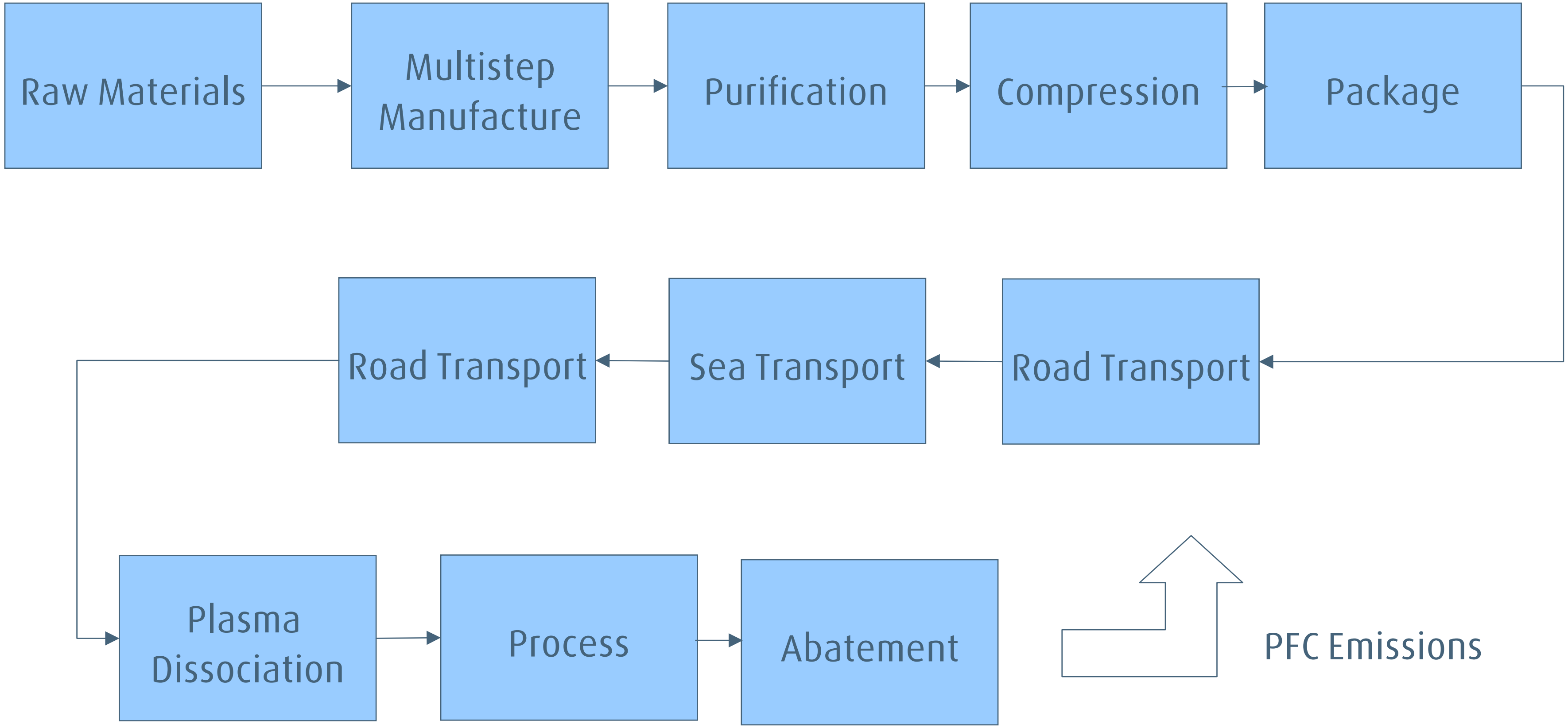
Issues & Characterization	**Show Stopper**	**High Restriction Potential**	**Medium Restriction Potential**
List of Chemicals or Raw Materials Subject to Actual or Potential Manufacture or Use Restrictions	Asbestos Materials Certain glycol ethers Polychlorinated biphenyls Fully halogenated chlorofluorocarbons (CFCs) Carbon tetrachloride 1,1,1 trichloroethane Halons 1211, 1301, 2402 Hydrobromofluorocarbons (HBFCs) HCFC 141b Polybrominated biphenyls (PBBs) and their ethers/oxides (PBDEs) Cadmium compounds Lead compounds Mercury compounds Hexavalent Chromium compounds Polychlorinated Biphenyls (PCB)/ Terphenyls (PCT) Polychlorinated Naphthalene (PCN) Short Chain Chlorinated Paraffins (C10-13, Cl >50%) Tributyl tin (TBT) and, Triphenyl tin (TPT) compounds Certain Azo Colorants	Hydrochlorofluorocarbons (HCFCs) Perfluorooctyl sulfonates (PFOS) Cadmium compounds Lead compounds Mercury compounds Hexavalent Chromium compounds Other chlorinated organic compounds Other brominated organic compounds	Perfluorocompounds (PFCs) - SF6 - C4F10 - C2F6 - C5F12 - CF4 - C6F14 - NF3 - C4F8 - CHF3 - C3F8 Hydrofluorocarbons (HFCs) Perfluorooctanoic acid (PFOA) and its salts Certain phthalates Phenols Perfluoroalkyl sulfonates (PFAS) Ethylene Oxide Ethylene Dichloride Polyaromatic hydrocarbons Antimony Trioxide Beryllium Polyvinyl chloride (PVC) Other brominated flame retardants

Why Fluorine for dry cleaning?

Better for the environment.

Clean Gas	Atmospheric Lifetime (Years)	Global Warming Potential (GWP_{100})
CF_4	50,000	6,500
C_2F_6	10,000	9,200
C_3F_8	2,600	7,800
SF_6	3,200	23,900
NF_3	740	10,800
C_5F_8	0.98	90
COF_2	1	1
C_3F_6	<<1	<1
F_2	0	0

NF_3 Energy Footprint



Raw Materials

Multistep Manufacture

Purification

Compression

Package

Road Transport

Sea Transport

Road Transport

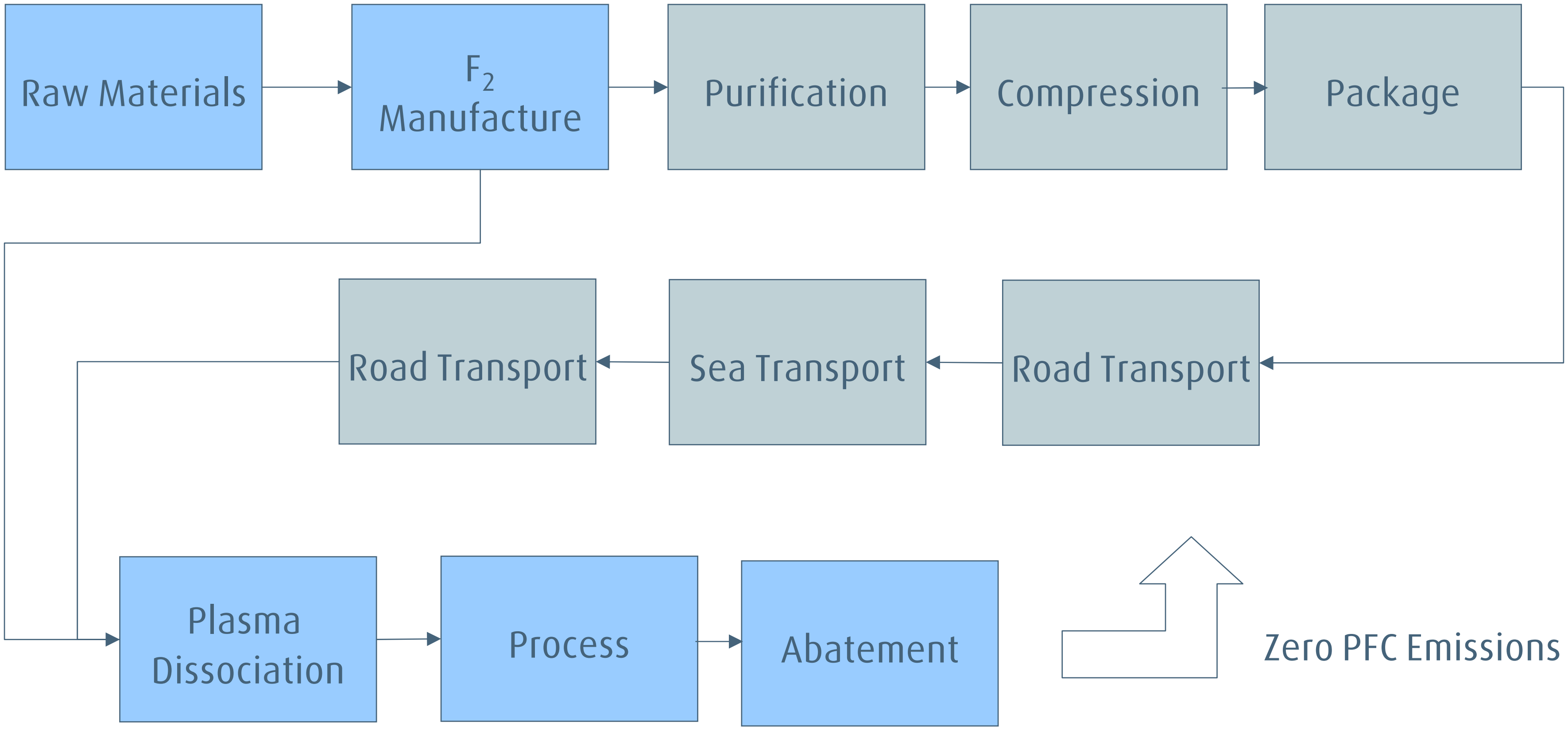
Plasma Dissociation

Process

Abatement

PFC Emissions

F_2 Energy Footprint



Raw Materials

F_2 Manufacture

Purification

Compression

Package

Road Transport

Sea Transport

Road Transport

Plasma Dissociation

Process

Abatement

Zero PFC Emissions

Why Fluorine for dry cleaning?

More cost effective

1.5 moles F_2 required to produce same amount free Fluorine as 1 mole of NF_3 or ClF_3

50% higher flow F_2 required compared to NF_3 to provide same number of Fluorine radicals

Gas is typically sold by weight – greater cleaning performance provided per kg F_2

Molecular mass F_2 = 38 * 1.5 = 57

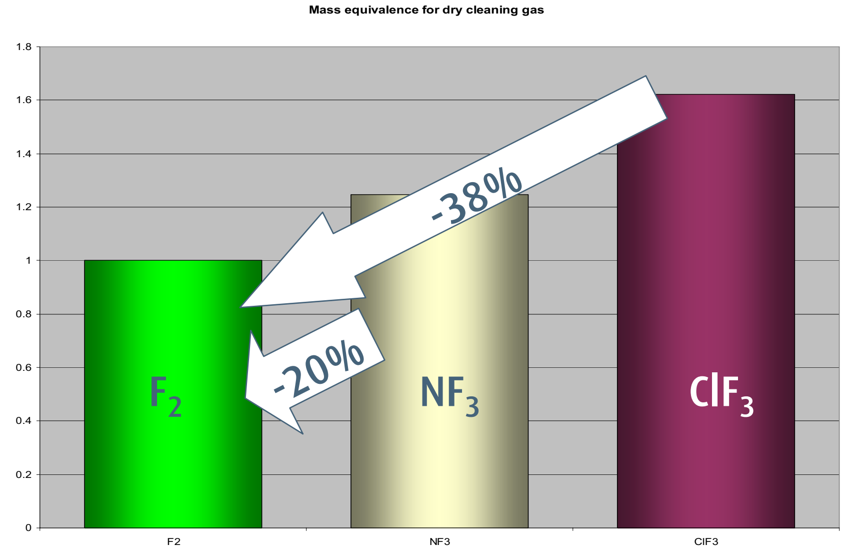
Molecular mass NF_3 = 71

Molecular mass ClF_3 = 92.5

1kg F_2 provides same mass of F radicals as

1.25kg NF_3

1.62kg ClF_3



If we assume same cost per kg, significant material cost savings possible, but

- NF_3 manufacture generally uses F_2 gas as a feedstock, so direct electrolysis of F_2 from HF is inherently cheaper
- NF_3 / ClF_3 must be purified, packaged and shipped

1kg on-site generated F_2 is not more expensive than 1kg cylinder NF_3 or ClF_3

On-site F_2 for dry cleaning
Process Experience

Thermal clean for 300mm LPCVD – developed since 2002

- Improved selectivity demonstrated compared to ClF_3
- Improved etch rate (shorter cleaning time) compared to NF_3
- Lower temperature cleaning compared to NF_3
- No difference in etch rates or clean effects observed compared to cylinder F_2
- No restrictions in clean time due to cylinder size
- 100% F_2 available for cleaning – blending option available to meet any process requirement
- Higher purity - potential benefits for film quality and / or clean frequency

> **“We have experienced good cleaning performance in the process developed for the TELFORMULA tool using BOC on-site fluorine generation system”**
>
> Source: Yasuyuki Kuriki, TEL VP and GM, thermal processing systems. TEL press release Sep-04

Currently used in high volume 300mm production in :

Korea, China, Singapore, France

Extension to PECVD Chamber Cleaning

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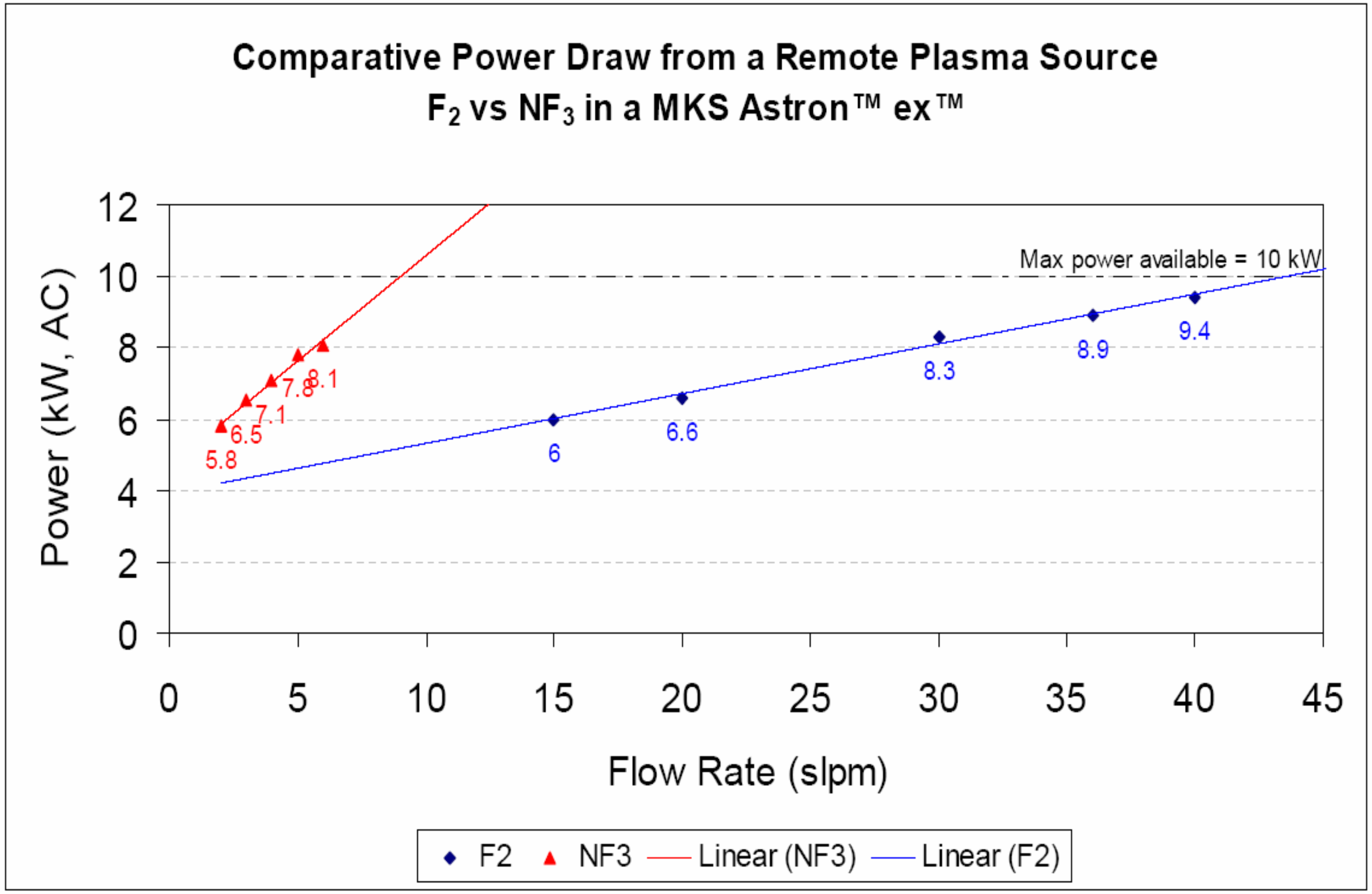
Activation of Fluorine Cleaning Gases

Limitations of NF_3 in an MKS Astron RPS

Investigating F_2 flows for a customer at our San Marcos R&D Facility – we found a significant increase in F_2 flow is possible in the RPS.

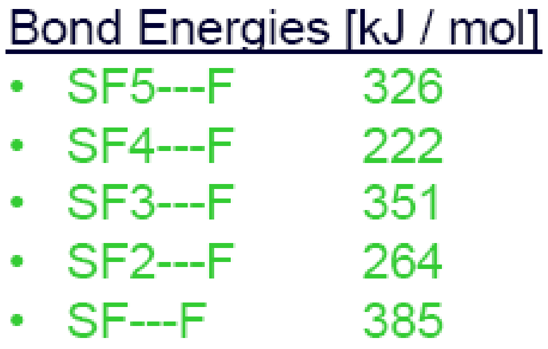


Activation of Fluorine Cleaning Gases

Bond Energies require high energy input for PFCs

Bond Energies [kJ / mol]

F---F	159
F_2N---F	248
FN---F	278
N---F	316



Bond Energies [kJ / mol]

SF5---F	326
SF4---F	222
SF3---F	351
SF2---F	264
SF---F	385

From Linde Astron Experiments: Limit of Throughput @ 10 kW Input Power

F_2: 44 slm

= 1.96 mol / min
(1.96 mol / min) x (159 kJ / mol)
= 312 kJ / min = **5.2 kW for 3.9 mol / min F·**

NF_3: 9 slm

= 0.401 mol / min
(0.401 mol / min) x (248 kJ / mol + 278 kJ / mol + 316 kJ / mol)
= 338 kJ / min = **5.6 kW for 1.2 mol / min F·**

> 3x F* at maximum flows from F_2 vs. NF_3

THEORETICAL BOND ENERGY SUPPORTS HIGH FLOW CAPABILITY SEEN ON RPS EXPERIMENTS

MKS Astron ex™ RPS

NF_3 v F_2 Flow/Pressure Operating Windows

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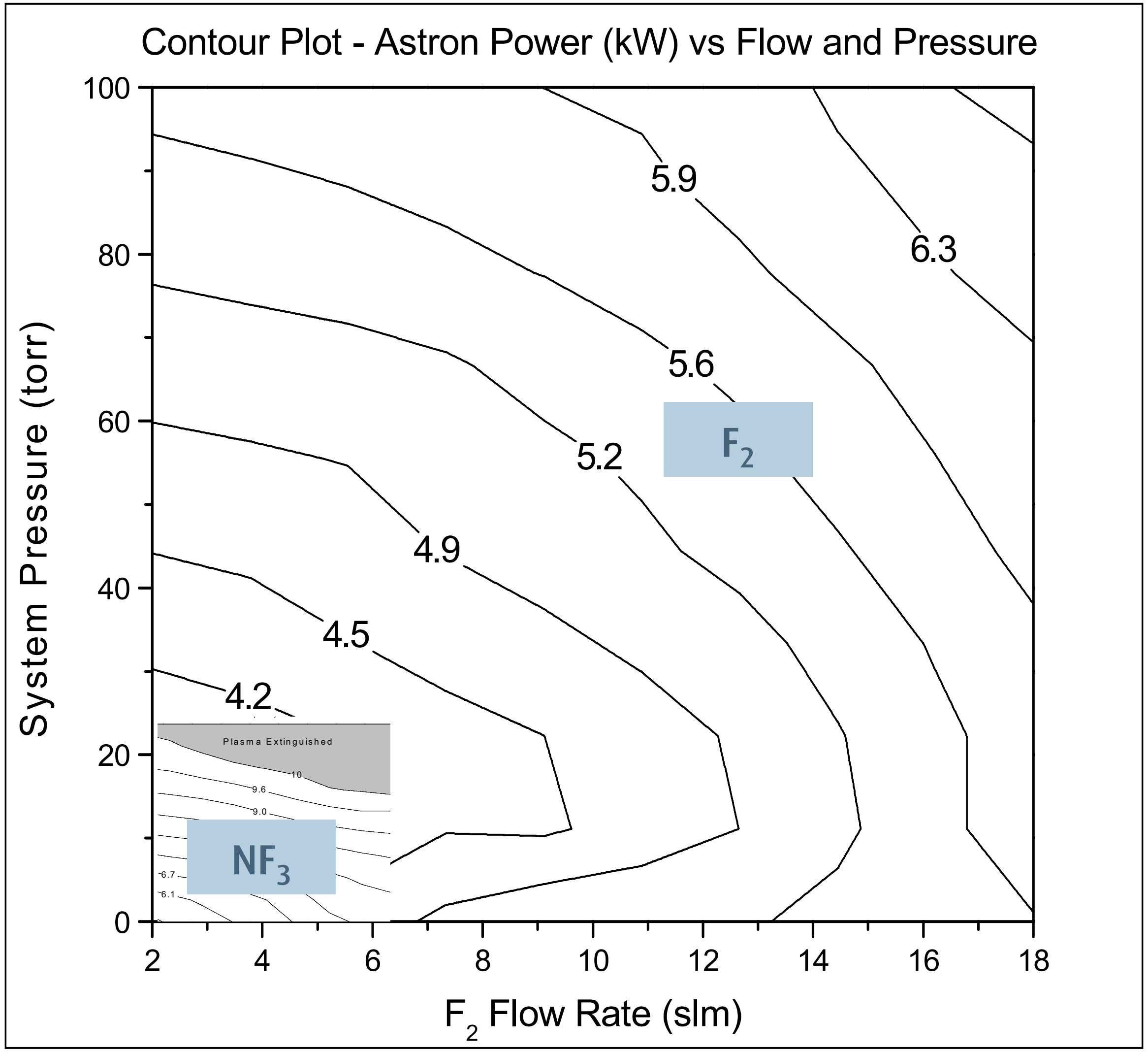
F_2 is much easier to form a plasma than NF_3

- At full RPS power, 3.3 X the F content can be used

	F_2	NF_3
Bond strength (kJ/mol)	F-F 159	F_2N-F 248 FN-F 278 N-F 316
Activation Energy for 1 mol F*	80 kJ	281 kJ



Process Benefits to Customer - Summary

•Plasma cleaning rate for large PECVD chambers is limited by high energy required to dissociate NF_3.

•Fluorine overcomes this limitation in any size plasma source and allows higher flows of clean gas to improve productivity at a lower power.

•In Gen 6 production on a range of process tools, fluorine has been demonstrated to

- Reduce clean times by 30% compared to NF_3 (flow restrictions prevent further demonstrated improvements)
- Reduce mass consumption by 20% (6 tons / month NF_3 replaced by 5 tons / month F_2)
- Reduce RPS power consumption by >50%
- Increase the interval between cleans

•There is no difference in film quality or end product quality from F_2 cleaning compared to NF_3 cleaning

- For Thin Film Solar applications, the absence of N inclusions is reported to be very advantageous

Extension to PECVD Semicon (Solvay)

Microsoft
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F_2 mixtures as chamber cleaning gas for PECVD systems not RPS assisted

Those systems are still responsible for high greenhouse emissions. F_2 mixtures offer a market available alternative which is environmentally friendly, fully compatible, cost effective and which enhances throughput.

Alternative chamber cleaning with F_2 for semiconductors

Project Target:	**Feasibility study for the use of F_2 as a chamber cleaning gas with an industrially used plasma-CVD reactor (AMAT P 5000)**
Motivation:	**Reduce global warming emissions caused by NF_3 or carbon-fluorides used for chamber cleaning**
Location:	**Fraunhofer IZM, Munich; CMOS compatible class 10 clean room**
Equipment:	**Applied Materials (AMAT) P 5000 platform, lamp-heated, plasma-enhanced CVD chamber for dielectric films**
Wafer Size:	**200 mm**
Film Types:	**Silane-based PECVD of SiO_2 and Si_3N_4**

Results from repeatability runs

$Ar/F_2/N_2$ Clean Recipe: appr. 1,5 x faster than AMAT BKM Clean (CF_4)
appr. 1,2 x faster than NF_3 BKM Clean

Low particle values: < 50 adders - as good as with CF_4 Clean

Wafer-to-Wafer Non-Uniformity 0,6 % - identical to AMAT BKM Clean

Within-Wafer Non-Uniformity: 1,6 % - identical to AMAT BKM Clean

Chamber, Shower Head and Susceptor OK after visual inspection

$Ar/F_2/N_2$ cleaning gas mixture fully usable with AMAT P 5000 CVD chamber

Comparison of different cleaning chemistries

Cleaning gas	SiO2 Etch Rate [nm/min]	Unif. [%] 1sigma	Si3N4 Etch Rate [nm/min]	Unif. [%] 1sigma	Total Flow [sccm]	Clean Gas Flow [sccm]	Clean Gas Flow [gr/min]	Net F-amount [g/min]	Pressure [Torr]	RF-Power [W]	Sucs. Spacing [mils]
ArN2F2	**1521**	**12**	**1950**	**8**	900	180	0.31	**0.31**	2.1	800	570
CF4	**850**	**2**	**1710**	**9**	2005	1550	6.09	**5.26**	5.5	1000	570
NF3	**≤ 1200**	**20**	**≤ 1570**	**20**	150	150	0.48	**0.38**	0.6	600	570
C2F6/O2/NF3 (Average)	**1116**	**10**	**1303**	**40**							
C2F6/O2/NF3 (Outer Clean)	439	11	716	47	1560	750 / 60	4.62/0,19	3.96	1.8	900	1000 *
C2F6/O2 (Inner Clean)	1792	8	1890	33	1850	900	5.54	4.58	9.0	900	200
NF3 clean limited by etch uniformity											
NF3	**932**	**9**	**1300**	**20**	140	140	0.44	0.36	0.6	350	800 **

*Max spacing of universal-chamber ; dielectric CVD chambers are limited to 570 mils

**Max spacing of W-chamber ; dielectric CVD chambers limited to 570 mils

Comparison of different cleaning chemistries
- Gas consumption -

		SiO_2			Si_3N_4		
Cleaning gas	Layer Thickness [µm]	Cleaning Time [sec]	Required gas [gr]	Required gas % vs. F2	Cleaning Time [sec]	Required gas [gr]	Required gas % vs. F2
ArN_2F_2	1.0	47.3	0.245	**100%**	36.9	0.191	**100%**
CF_4	1.0	84.7	8.598	**3515%**	42.1	4.274	**2240%**
NF_3	1.0	60.0	0.480	**196%**	45.9	0.367	**192%**

Cleaning time includes a 20 % overclean time to make shure all areas of the chamber are cleaned

Summary

F_2 provides the following benefits for PECVD chamber cleaning:

- Zero environmental impact & reduced power consumption – an environmentally responsible choice
- Process throughput increase – reduced clean time.
- More cost effective cleaning, lower material bill, reduced power consumption
- Reliable and safe operations, fully proven in the semiconductor and flat panel display industries

By adopting F_2 gas, TMD will be contributing to the reduction of greenhouse gas emissions (based on the amount of CO_2 emissions) to zero from the cleaning process, whereas with NF_3 gas, zero gas emissions could not be achieved, even with detoxifying systems. *Toshiba Matsushita Display Technology Press Release 19-Sep-06*

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Thank you for your attention

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