
Green Processes for low cost and high productivity
绿色制程带来低成本与高生产力
Solarcon China. March 2010

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Fluorine Environmental Benefit

氟气对环境的好处

What do we mean by “Green”?
您的产品被称为 « 绿色 » ?

Is your product “Green” only because it uses less energy?

Is your process “Green” because you can’t detect any emissions from your factory?

An electric car is only as clean as the power station that generates it’s power!

Clean?

Green?

The full supply chain and product lifecycle must be considered: Energy use, environmental impact for all elements of the supply chain.

The same is true for Green House Gases.....

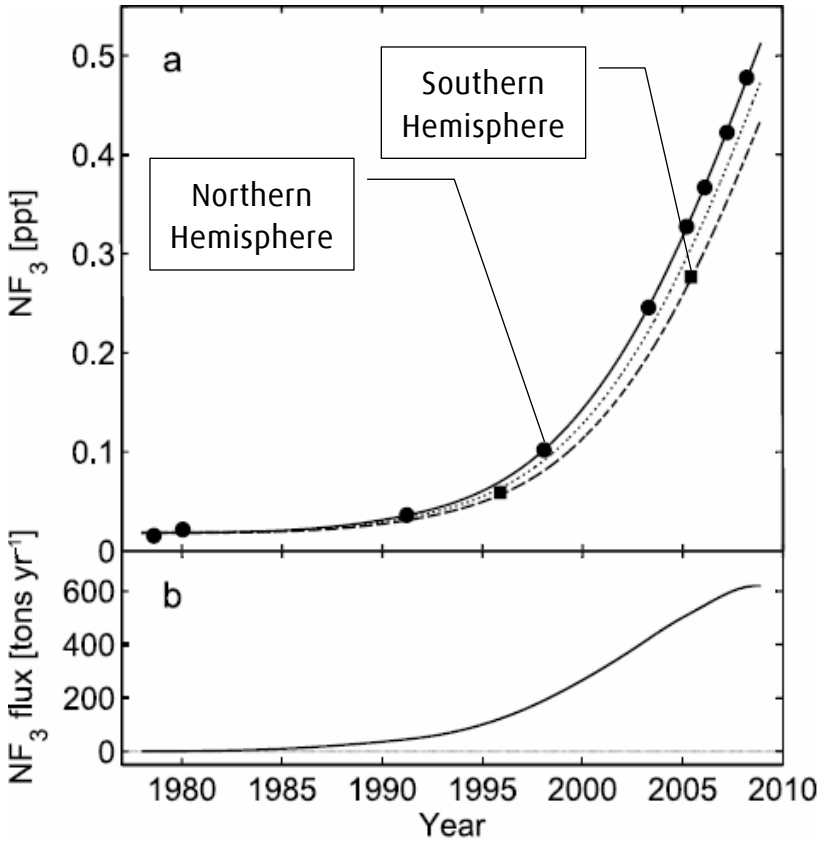
Trend to regulate Green House Gas Emissions from silicon processing

June 2008: Michael Prather identifies NF_3 as "The Greenhouse Gas Missing from Kyoto"
« NF3, 京都议定书中遗漏的温室气体 »

October 2008: Scripps Institute measure NF_3 in the atmosphere,
~16% of global capacity is vented!

April 2009: US EPA legislation requires use and emissions monitoring for every process using GHGs.

UNIPCC – NF_3 is expected to be listed as a GHG.



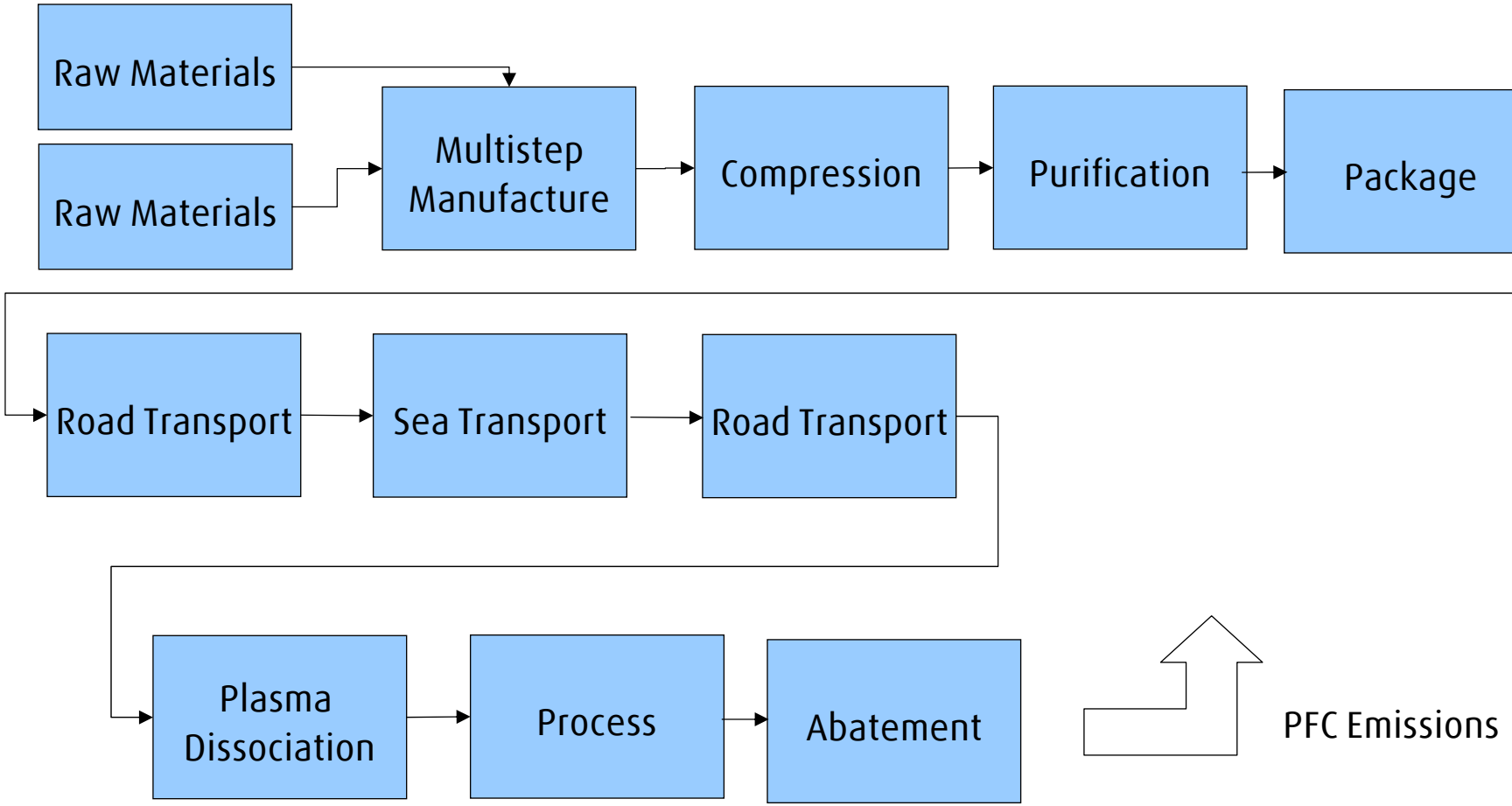
Legislation usually is developed to address OVERALL ACTUAL measured emissions of the material, from the entire industry, not just the point of use!

Semiconductor Industry Driving Forces
ITRS ESH 2007 – Risk of restriction of Chemical use

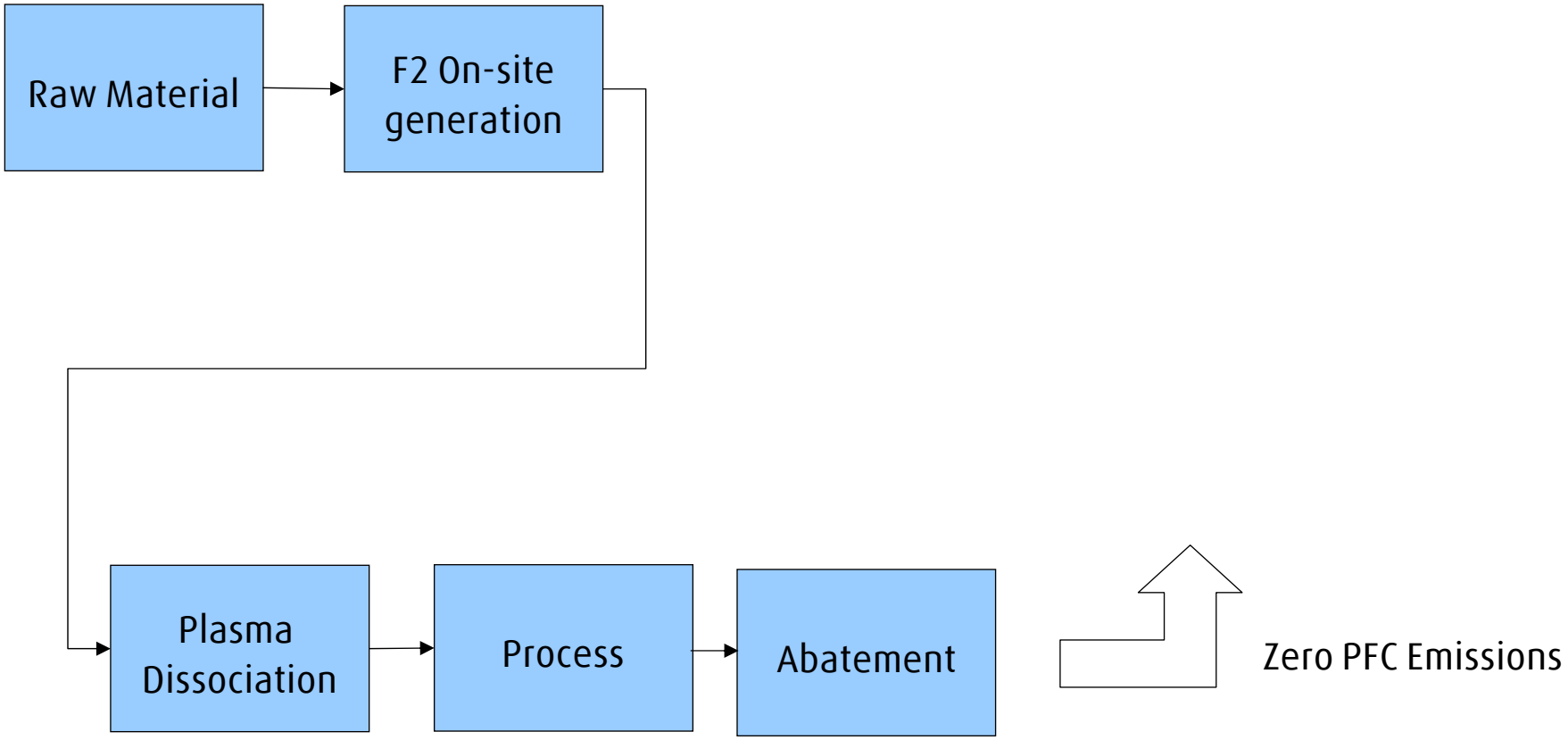
Issues & Characterization	Show Stopper	High Restriction Potential	Medium Restriction Potential
List of Chemicals or Raw Materials Subject to Actual or Potential Manufacture or Use Restrictions	Asbestos Materials Certain glycol ethers Polychlorinated biphenyls Fully halogenated chlorofluorocarbons (CFCs) 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

Many typical cleaning gases may become restricted

NF_3 : Multistep Manufacture – Energy intensive



F_2 On-site Supply: Simpler process. More efficient, less capital intensive



CO2 equivalent savings from elimination of NF3

NF3 -> F2 larger scale customers: Malibu, Masdar, TMD and LG Display

Annual CO2 emissions eliminated from the cleaning gas supply chain:

= 350,000 tonnes/yr

According to Weiss et al. (16% of NF3 consumption X 17,200)

Every Hour, Linde prevents *40 tonnes* of CO2 equivalent emission reduction.

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	550	17,200
C_5F_8	0.98	90
COF_2	1	1
C_3F_6	<<1	<1
F_2	0	0

Solution: Fluorine Chamber Cleaning

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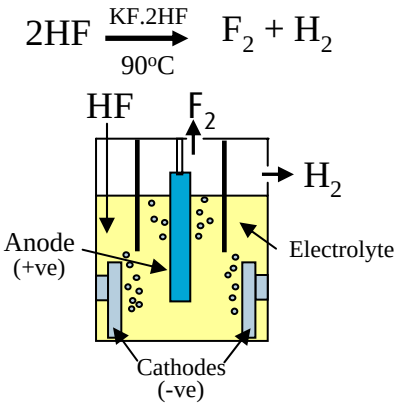
WHAT is Fluorine?

Fluorine is the active ingredient in all silicon chamber cleaning.

Fluorine gas (F_2) is a faster and environmentally friendly replacement for Greenhouse Gases like NF_3 used to clean waste silicon from ***Semicon, LCD and Solar CVD tools***

HOW do we deliver it?

Generation-*F*®
On-site Fluorine
Generation
Systems



WHY use Fluorine?

☑ **Productivity** Faster cleaning boosts output **7-12%** ,worth **€1.5/yr** to a typical Thin film solar customer

☑ **Cost Reduction** Direct material cost saving of **>20%**

☑ **Environment** F_2 has **Zero** Global Warming Potential, while NF_3 is **17.200 x CO_2**

Solution: On-site Fluorine,
模组化设计, 可依据用量而扩充

300 mm Wafer
半导体十二寸晶圆厂

Gen 4 TFT-LCD

Gen 6 TFT-LCD

Gen 8 TFT-LCD
平面显示器

1 tonne/yr

>10 tonnes/yr

100's tonnes/yr

Cleaning Performance = Productivity

氟气在制程上的好处=高产出(高处理量)

On-site F_2 for Semiconductor dry cleaning:
Process Experience since 2002

Thermal clean for 300mm LPCVD

在半导体的主要应用是批次式LPCVD制程设备的干式清洁(热分解)

Improved selectivity demonstrated compared to ClF_3

Improved etch rate (shorter cleaning time) compared to NF_3

Reduced downtime compared to wet cleaning.

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

→ Currently used in high volume 300mm production in : Korea, China, Singapore, France

→ OEM qualified and approved

Movement to extend on-site F_2 to PECVD chamber cleaning in semiconductor

将氟气产生器的应用扩展到半导体PECVD的腔体清洁...

Fluorine Process Benefits in PECVD Cleaning: A Combination of Thermodynamics (Energy) and Kinetics (Chemical Pathways)

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Thermodynamics

F2 takes much less energy to produce F· radicals than NF3 or SF6

Bond Energies [kJ / mol]					
F2		**NF3**		**SF6**	
F---F	**159**	**F2N---F**	**248**	**F5S---F**	**326**
		FN---F	**278**	**F4S---F**	**222**
		N---F	**316**	**O---O**	**249**

- → F· from F2: 60 kJ / mol
- → F· from NF3: 281 kJ / mol
- → F· from SF6: 399 kJ / mol

Kinetics (in-situ)

F2 has only one pathway in a plasma dissociation

$F_2 \rightarrow F\cdot + F\cdot$

It is kinetically forbidden for two atoms, like 2 F·, to recombine in the gas-phase

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NF3 has two competing pathways

1. $NF_3 \rightarrow NF_2 + F\cdot$

2a. $NF_2\cdot \rightarrow NF + F\cdot$

2b. $NF_2\cdot + NF_2\cdot \rightarrow N_2F_4$

As process conditions tend to higher flows and rf power, pathway 2b predominates

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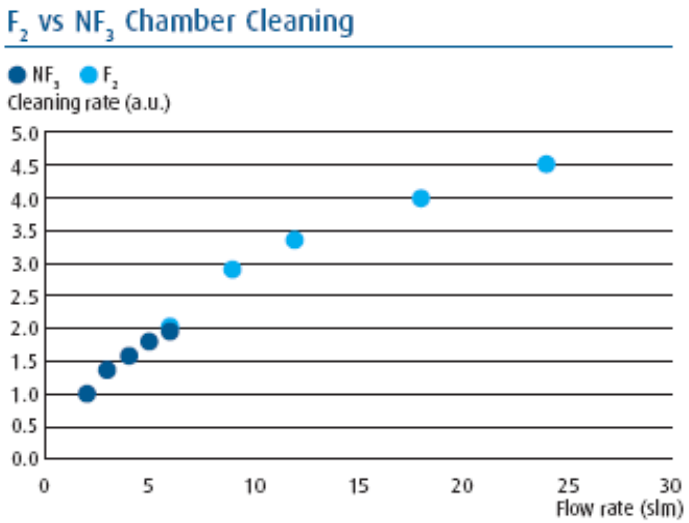
O2 is added to SF6 plasmas to prevent sulfur deposits

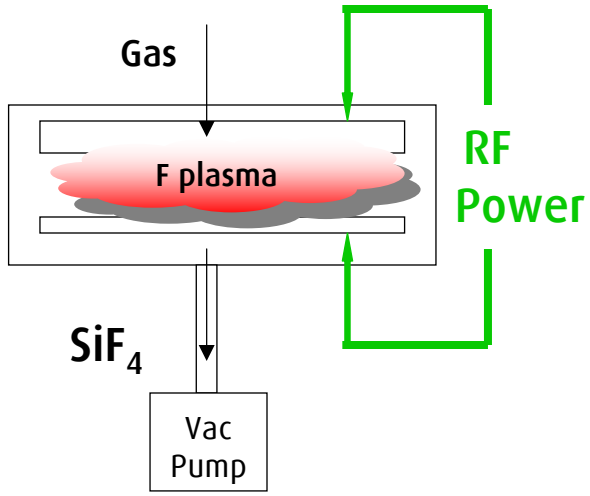
$SF_6 + \frac{1}{2}\,O_2 \rightarrow SOF_4 + 2\,F\cdot$

The predominant pathway greatly limits efficiency

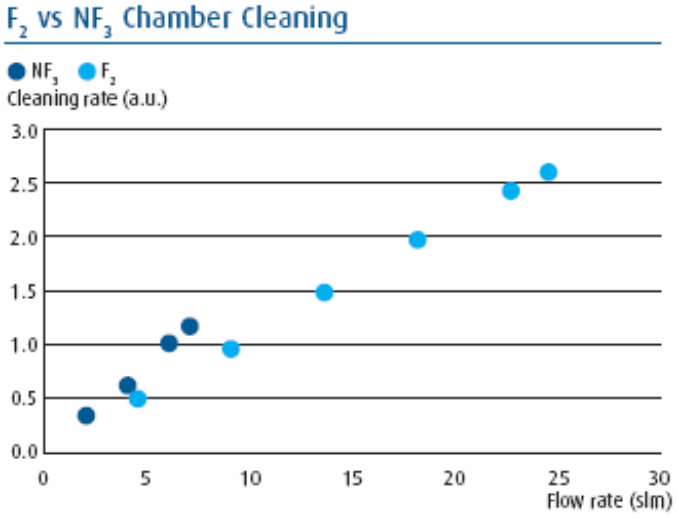
High Performance PECVD Chamber cleaning

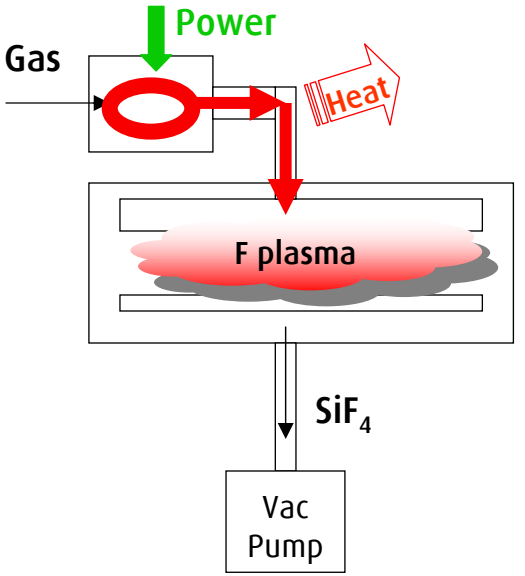
In-situ Plasma





Remote Plasma





Fluorine Process Benefits: Cleaning Speed in PECVD: Summary of Actual Process Results

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RPS Activation

	F2	NF3
Mass Efficiency[a]	~100 %	80%
Cleaning Speed[b]	3x +	1x
Energy Consumption[c]	985 kWh / ton	2640 kWh / ton

In Situ Activation

	F2	NF3	SF6
Mass Efficiency[d]	~100 %	55%	26%
Cleaning Speed[e]	5x +	1.7x	1x
Energy Consumption[f]	3280 kWh / ton	9580 kWh / ton	7110 kWh / ton

*source:

a) Malibu/Linde F2 tests at Bielefeld (AKT)
b) Malibu/Linde F2 tests at Bielefeld (AKT), Linde F2 tests at ITRI (AKT)
c) Malibu/Linde F2 tests at Bielefeld (AKT), Malibu/Linde F2 tests at Bielefeld (KAI)
d) Linde F2 tests at NexPower (Ulvac) / Linde F2 test at Bielefeld (KAI)
e) Oerlikon presentation at PVSEC09, Linde F2 tests at NexPower (Ulvac), Malibu/Linde F2 tests at Bielefeld (KAI)
f) Linde F2 tests at NexPower (Ulvac), Malibu/Linde F2 tests at Bielefeld (KAI)

3rd Party Verification of Cleaning Performance:

- **Publications on F2 Cleaning Speed, etch rate etc.**

- **Display:**
  - AKT Display: Published testing results FPD International, Yokohama, 2008

- **Solar:**
  - AIST Japan: Published in-situ clean test results for solar
  - Malibu PV published F2 performance results from their trials on Applied solar equipment

- **Semiconductor:**
  - Fraunhofer Institute – etch rate studies
  - Solvay Fluor, Infineon – etch rate studies

Cost Reduction

降低成本

Fluorine Process Benefits: Mass saving

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RPS Activation

	F2	NF3
Mass Efficiency[a]	~100 %	80%

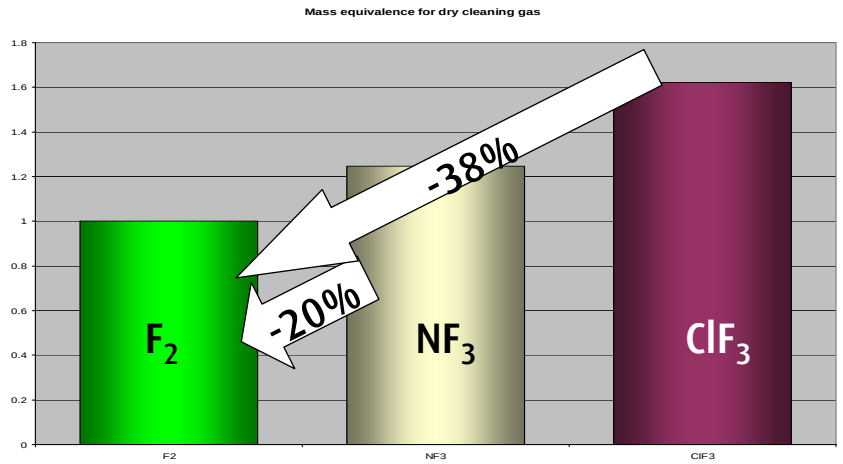
In Situ Activation

	F2	NF3	SF6
Mass Efficiency[b]	~100 %	55%	26%

1.5 moles F2 required to produce same amount free Fluorine as 1 mole of NF3 or ClF3

50% higher flow F2 required compared to NF3 to provide same number of Fluorine radicals

BUT: 气体销售的单位不是以体积而是以重量



在完全解离的情况下, 1Kg F2, 1.25Kg NF3, 与 1.62Kg ClF3所能提供的氟自由基数量是相同的

*source:

a) Malibu/Linde F2 tests at Bielefeld (AKT)

b) Linde F2 tests at NexPower (Ulvac) / Linde F2 test at Bielefeld (KAI)

CONCLUSION

结论

Replacing NF_3 with On-site fluorine - addresses key throughput, cost & environmental concerns

Faster cleaning, higher productivity

- Fluorine can clean twice as fast as NF_3 with 10% lower mass consumption
- Can increase line throughput from 3.5-10%

Reduced gas consumption

- 80Kg of F_2 delivers the same cleaning as 100 Kg of NF_3 with the same clean rate

Lower environmental impact

- F_2 has **zero** global warming potential vs. 17,000 for NF_3
- 60% Reduced electricity consumption in plasma source

Modular On Site Solution:
Eliminates logistics of trailer supply chain and guarantees security of supply

CONCLUSION

Thanks for your attention,

Time for your questions / 提问时间...

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The power behind tomorrow's technology