



## Fluorine :

Optimised and sustainable cleaning agent for CVD processes

THE LINDE GROUP

*Linde*

Plasma Etch Users Group Meeting  
15<sup>th</sup> May, 2008.

# Confidentiality Statement



THE LINDE GROUP

*Linde*

This presentation has been prepared exclusively for the benefit and use of The Linde Group and does not carry any right of publication or disclosure, in whole or in part, to any other party.

This presentation is the property of The Linde Group. Neither this presentation nor any of its contents may be used for any purpose without the prior written consent of The Linde Group.

The Linde Group makes no representations as to the accuracy, completeness or fairness of this presentation and so far as is permitted by law, no responsibility or liability whatsoever is accepted by The Linde Group for the accuracy or sufficiency thereof or for any errors, omissions, or misstatements relating thereto.

The Linde Group makes no express or implied product warranties on the basis of this presentation.

# Outline

THE LINDE GROUP

The Linde logo, featuring the word "Linde" in a white, elegant script font, set against a dark blue background with a light blue wavy line above it.

Industry driving forces

Potential benefits of F<sub>2</sub>

Cleaning for LPCVD

Cleaning for PECVD

Discussion of results / next steps

Summary

# Industry Driving Forces

## ITRS ESH 2007 extracts

THE LINDE GROUP

The Linde logo, featuring the word "Linde" in a white, cursive script font, set against a dark blue background with a light blue wavy line above it.

### 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<sub>2</sub> equivalent emissions*

# Industry Driving Forces

## ITRS ESH 2007 extracts

THE LINDE GROUP

The Linde logo, featuring the word "Linde" in a white, cursive script font, set against a dark blue background with a light blue wavy line above it.

### 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<sub>6</sub> 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

THE LINDE GROUP



### 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
<b>List of Chemicals or Raw Materials Subject to Actual or Potential Manufacture or Use Restrictions</b>	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.

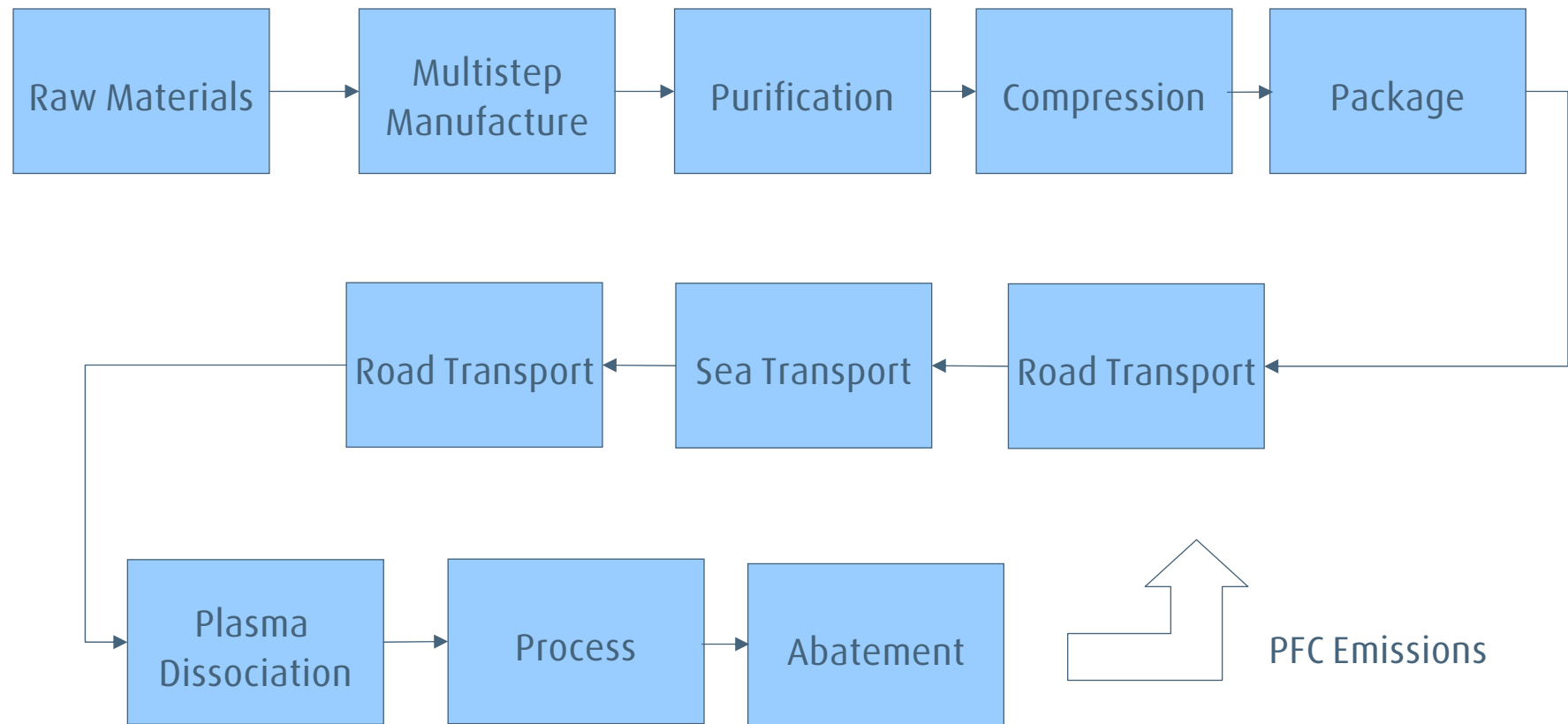
THE LINDE GROUP



Clean Gas	Atmospheric Lifetime (Years)	Global Warming Potential (GWP <sub>100</sub> )
CF <sub>4</sub>	50,000	6,500
C <sub>2</sub> F <sub>6</sub>	10,000	9,200
C <sub>3</sub> F <sub>8</sub>	2,600	7,800
SF <sub>6</sub>	3,200	23,900
NF <sub>3</sub>	740	10,800
C <sub>5</sub> F <sub>8</sub>	0.98	90
COF <sub>2</sub>	1	1
C <sub>3</sub> F <sub>6</sub>	<<1	<1
F <sub>2</sub>	0	0

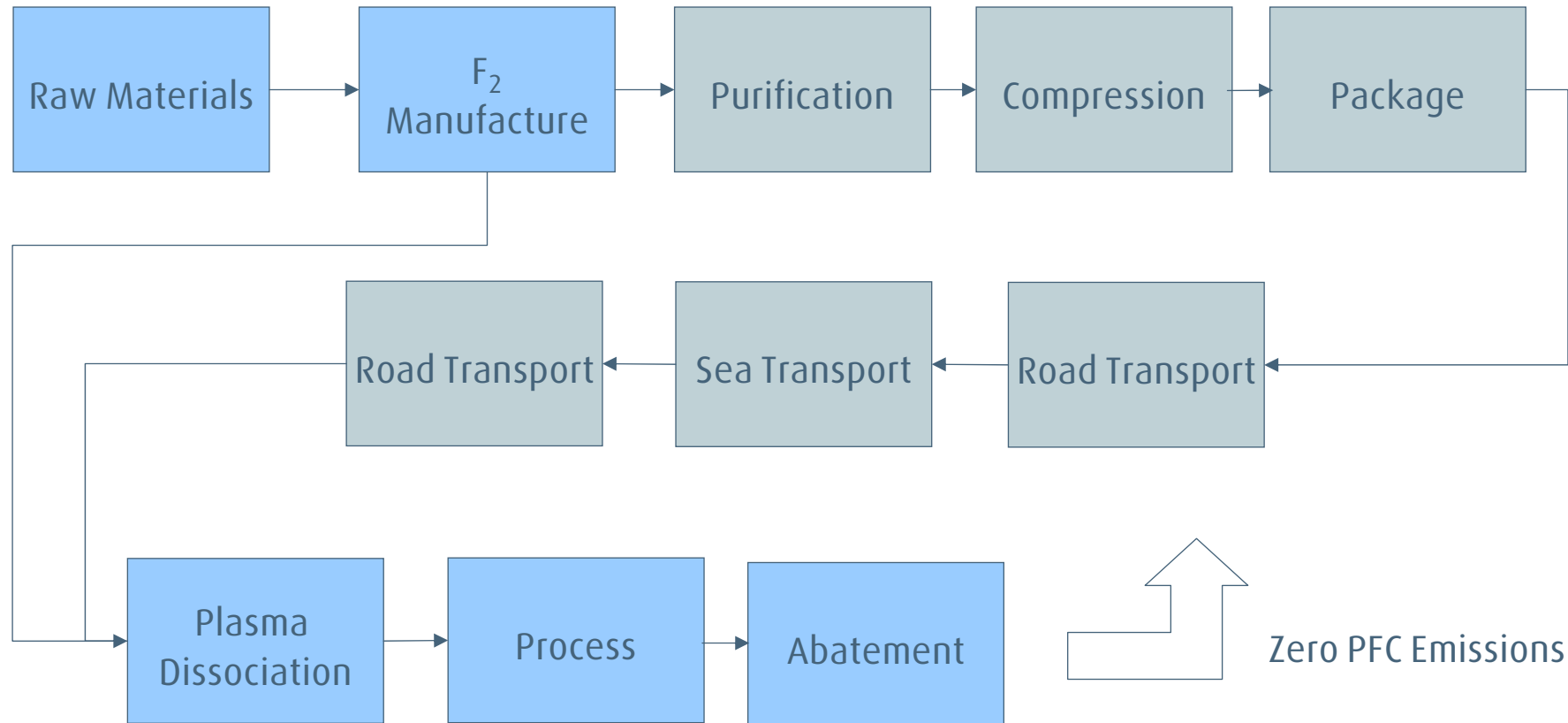
# NF<sub>3</sub> Energy Footprint

THE LINDE GROUP



# F<sub>2</sub> Energy Footprint

THE LINDE GROUP



# Why Fluorine for dry cleaning?

## More cost effective

THE LINDE GROUP

Linde

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  $F_2 = 38 * 1.5 = 57$

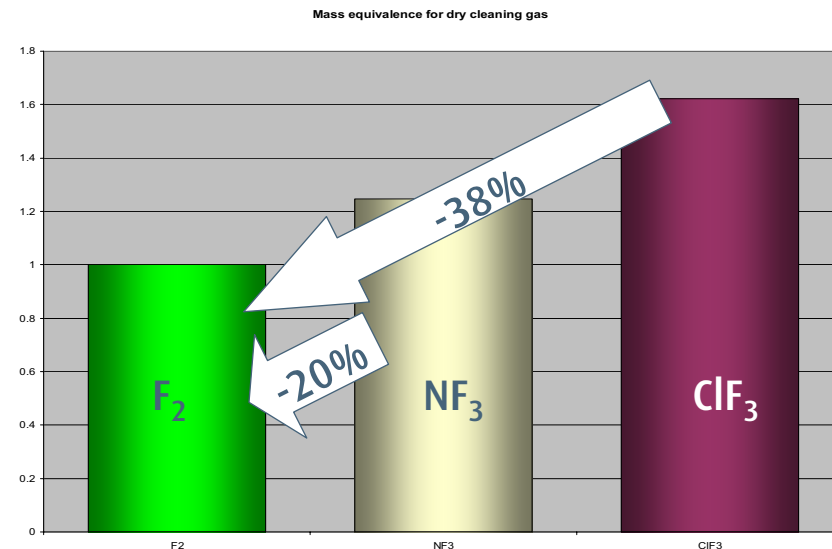
Molecular mass  $NF_3 = 71$

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<sub>2</sub> for dry cleaning

## Process Experience

THE LINDE GROUP



### Thermal clean for 300mm LPCVD – developed since 2002

Improved selectivity demonstrated compared to ClF<sub>3</sub>

Improved etch rate (shorter cleaning time) compared to NF<sub>3</sub>

Lower temperature cleaning compared to NF<sub>3</sub>

No difference in etch rates or clean effects observed compared to cylinder F<sub>2</sub>

No restrictions in clean time due to cylinder size

100% F<sub>2</sub> 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

THE LINDE GROUP

*Linde*

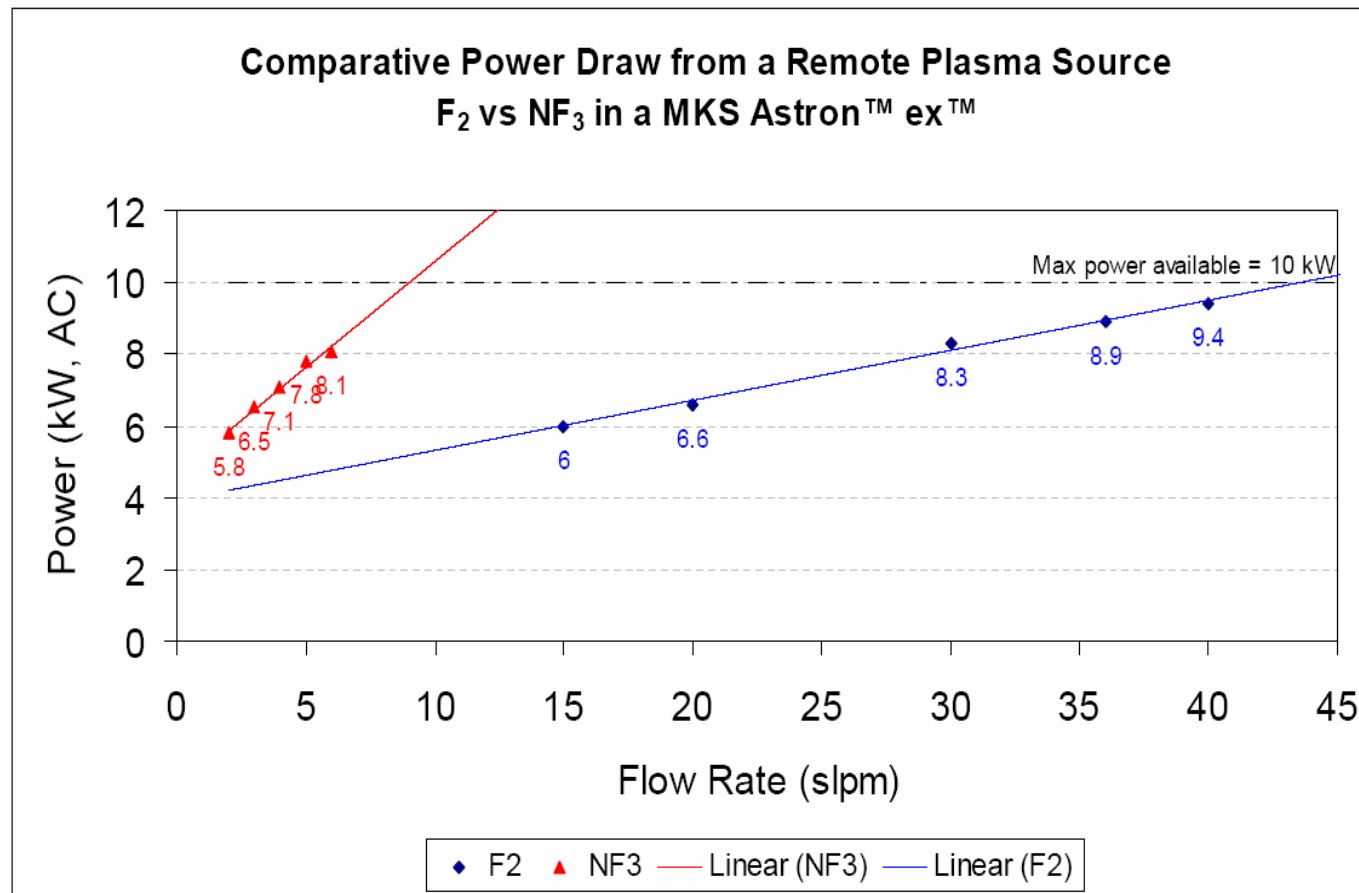
# Activation of Fluorine Cleaning Gases

## Limitations of $\text{NF}_3$ in an MKS Astron RPS

THE LINDE GROUP

Linde

Investigating  $\text{F}_2$  flows for a customer at our San Marcos R&D Facility – we found a significant increase in  $\text{F}_2$  flow is possible in the RPS.



# Activation of Fluorine Cleaning Gases

## Bond Energies require high energy input for PFCs

THE LINDE GROUP



### Bond Energies [kJ / mol]

<b>F---F</b>	<b>159</b>
F <sub>2</sub> N---F	248
FN---F	278
N---F	316

### Bond Energies [kJ / mol]

• SF <sub>5</sub> ---F	326
• SF <sub>4</sub> ---F	222
• SF <sub>3</sub> ---F	351
• SF <sub>2</sub> ---F	264
• SF---F	385

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

**F<sub>2</sub>: 44 slm**

$$= 1.96 \text{ mol / min}$$

$$(1.96 \text{ mol / min}) \times (159 \text{ kJ / mol})$$

$$= 312 \text{ kJ / min} = 5.2 \text{ kW for } 3.9 \text{ mol / min F}$$

**NF<sub>3</sub>: 9 slm**

$$= 0.401 \text{ mol / min}$$

$$(0.401 \text{ mol / min}) \times (248 \text{ kJ / mol} + 278 \text{ kJ / mol} + 316 \text{ kJ / mol})$$

$$= 338 \text{ kJ / min} = 5.6 \text{ kW for } 1.2 \text{ mol / min F}$$

> 3x F\* at maximum flows from F<sub>2</sub> vs. NF<sub>3</sub>

THEORETICAL BOND ENERGY SUPPORTS HIGH FLOW CAPABILITY SEEN ON RPS EXPERIMENTS

# MKS Astron ex™ RPS

## NF<sub>3</sub> v F<sub>2</sub> Flow/Pressure Operating Windows

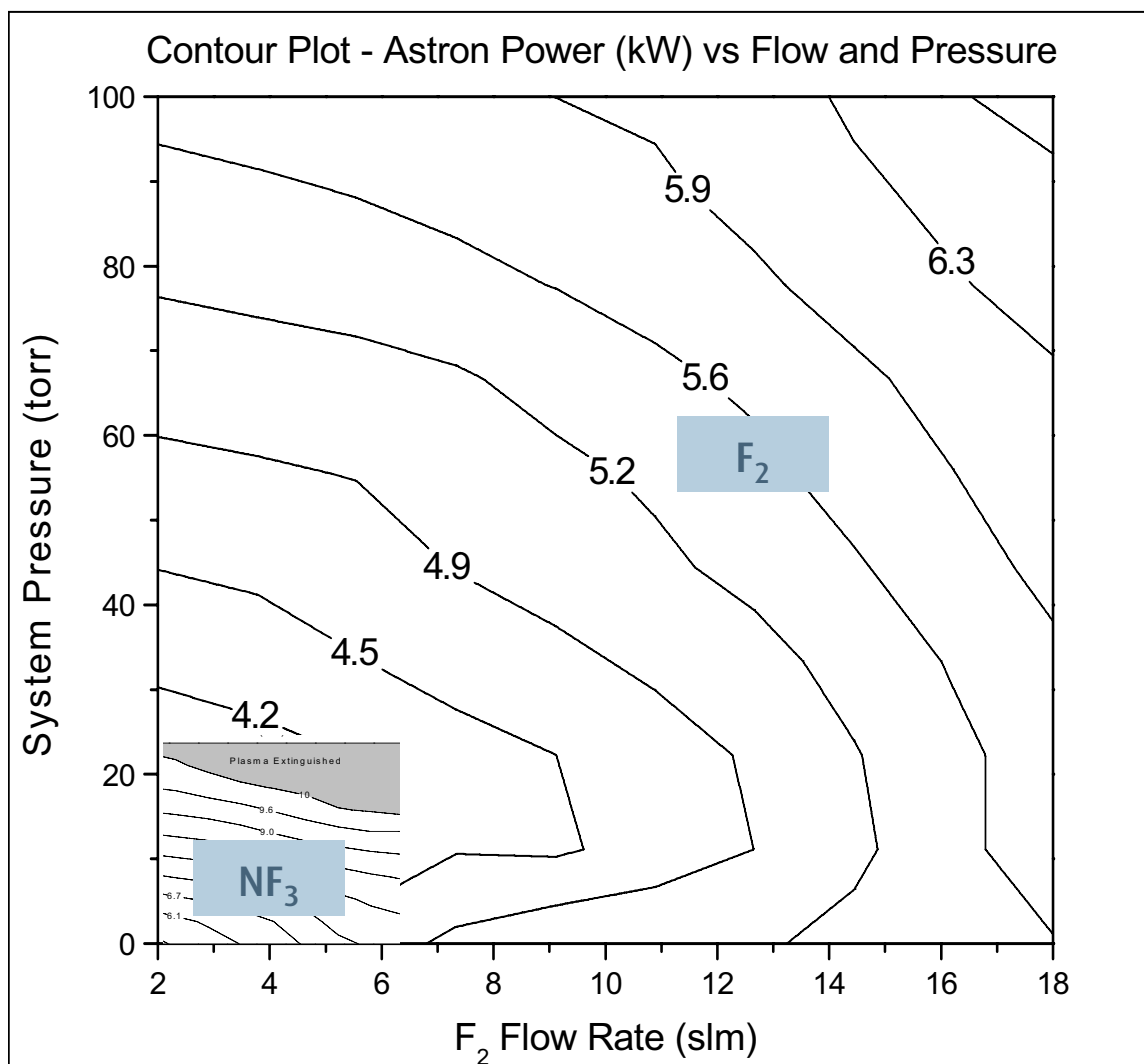
THE LINDE GROUP

Linde

F<sub>2</sub> is much easier to form a plasma than NF<sub>3</sub>

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

	F <sub>2</sub>	NF <sub>3</sub>
Bond strength (kJ/mol)	F-F 159	F <sub>2</sub> N-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  $\text{NF}_3$ .
- 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  $\text{NF}_3$  (flow restrictions prevent further demonstrated improvements)
  - Reduce mass consumption by 20% (6 tons / month  $\text{NF}_3$  replaced by 5 tons / month  $\text{F}_2$ )
  - Reduce RPS power consumption by >50%
  - Increase the interval between cleans
- There is no difference in film quality or end product quality from  $\text{F}_2$  cleaning compared to  $\text{NF}_3$  cleaning
  - For Thin Film Solar applications, the absence of N inclusions is reported to be very advantageous

# Extension to PECVD Semicon (Solvay)



Microsoft  
PowerPoint Presentati

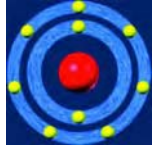
THE LINDE GROUP

*Linde*

## **F<sub>2</sub> mixtures as chamber cleaning gas for PECVD systems not RPS assisted**

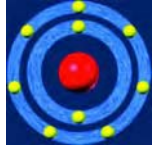
**Those systems are still responsible for high greenhouse emissions. F<sub>2</sub> mixtures offer a market available alternative which is environmentally friendly, fully compatible, cost effective and which enhances throughput.**





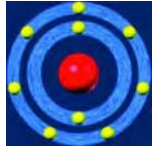
## Alternative chamber cleaning with F<sub>2</sub> for semiconductors

- Project Target:** Feasibility study for the use of F<sub>2</sub> as a chamber cleaning gas with an industrially used plasma-CVD reactor (AMAT P 5000)
- Motivation:** Reduce global warming emissions caused by NF<sub>3</sub> 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<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>



## Results from repeatability runs

- Ar/F<sub>2</sub>/N<sub>2</sub> Clean Recipe:**                      **appr. 1,5 x faster than AMAT BKM Clean (CF<sub>4</sub>)**  
**appr. 1,2 x faster than NF<sub>3</sub> BKM Clean**
- Low particle values:**                              **< 50 adders - as good as with CF<sub>4</sub> 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<sub>2</sub>/N<sub>2</sub> cleaning gas mixture fully usable with AMAT P 5000 CVD chamber**

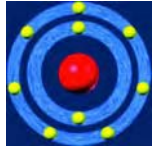


## Comparison of different cleaning chemistries

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]
<b>ArN2F2</b>	<b>1521</b>	<b>12</b>	<b>1950</b>	<b>8</b>	900	180	0.31	<b>0.31</b>	2.1	800	570
<b>CF4</b>	<b>850</b>	<b>2</b>	<b>1710</b>	<b>9</b>	2005	1550	6.09	<b>5.26</b>	5.5	1000	570
<b>NF3</b>	<b>≤ 1200</b>	<b>20</b>	<b>≤ 1570</b>	<b>20</b>	150	150	0.48	<b>0.38</b>	0.6	600	570
<b>C2F6/O2/NF3 (Average)</b>	<b>1116</b>	<b>10</b>	<b>1303</b>	<b>40</b>							
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
<b>NF3 clean limited by etch uniformity</b>											
<b>NF3</b>	<b>932</b>	<b>9</b>	<b>1300</b>	<b>20</b>	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 -

Cleaning gas	Layer Thickness [ $\mu\text{m}$ ]	$\text{SiO}_2$			$\text{Si}_3\text{N}_4$		
		Cleaning Time [sec]	Required gas [gr]	Required gas % vs. F2	Cleaning Time [sec]	Required gas [gr]	Required gas % vs. F2
$\text{ArN}_2\text{F}_2$	1.0	47.3	0.245	100%	36.9	0.191	100%
$\text{CF}_4$	1.0	84.7	8.598	3515%	42.1	4.274	2240%
$\text{NF}_3$	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

$F_2$  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*

## Contact Details



THE LINDE GROUP

*Linde*

Linde Electronics contact :

[greg.shuttleworth@boc.com](mailto:greg.shuttleworth@boc.com)

[paul.stockman@linde.com](mailto:paul.stockman@linde.com)

[electronicsinfo@linde.com](mailto:electronicsinfo@linde.com)

[www.linde.com/electronics](http://www.linde.com/electronics)

Solvay contact :

[mark.looney@solvay.com](mailto:mark.looney@solvay.com)

[Marcello.riva@solvay.com](mailto:Marcello.riva@solvay.com)

[www.solvaychemical.us](http://www.solvaychemical.us)



**SOLVAY**

Thank you for your attention

THE LINDE GROUP

*Linde*