Synergistic Effects of Gas Mixtures in a transformer-coupled toroidal plasma source for remote chamber cleaning

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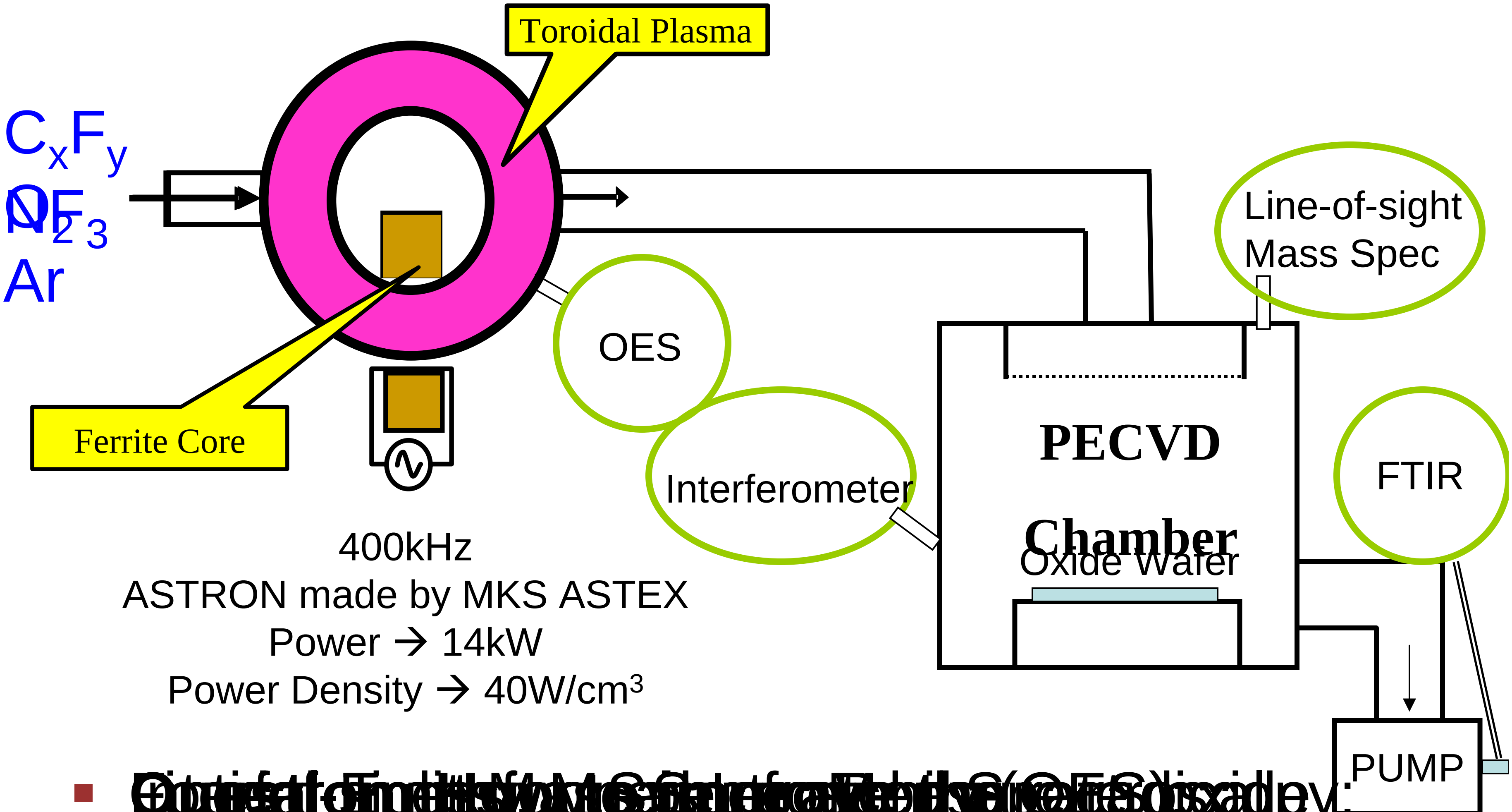
- Introduction of Equipments for Remote Chamber Cleaning
- Enhancement of Fluorocarbon Etching Rate by Nitrogen
  - Nitrogen prevents recombination to form COF_2
- Saturation of Etching Rate
  - P_F small : Linear regime → Increase NF3 Flow Rate
  - P_F large : Saturation regime → Increase Temperature
- Synergistic Effect of Gas Mixtures on Nitride Film
  - Enhancement of Etching Rate
  - NF_3 vs. Blend

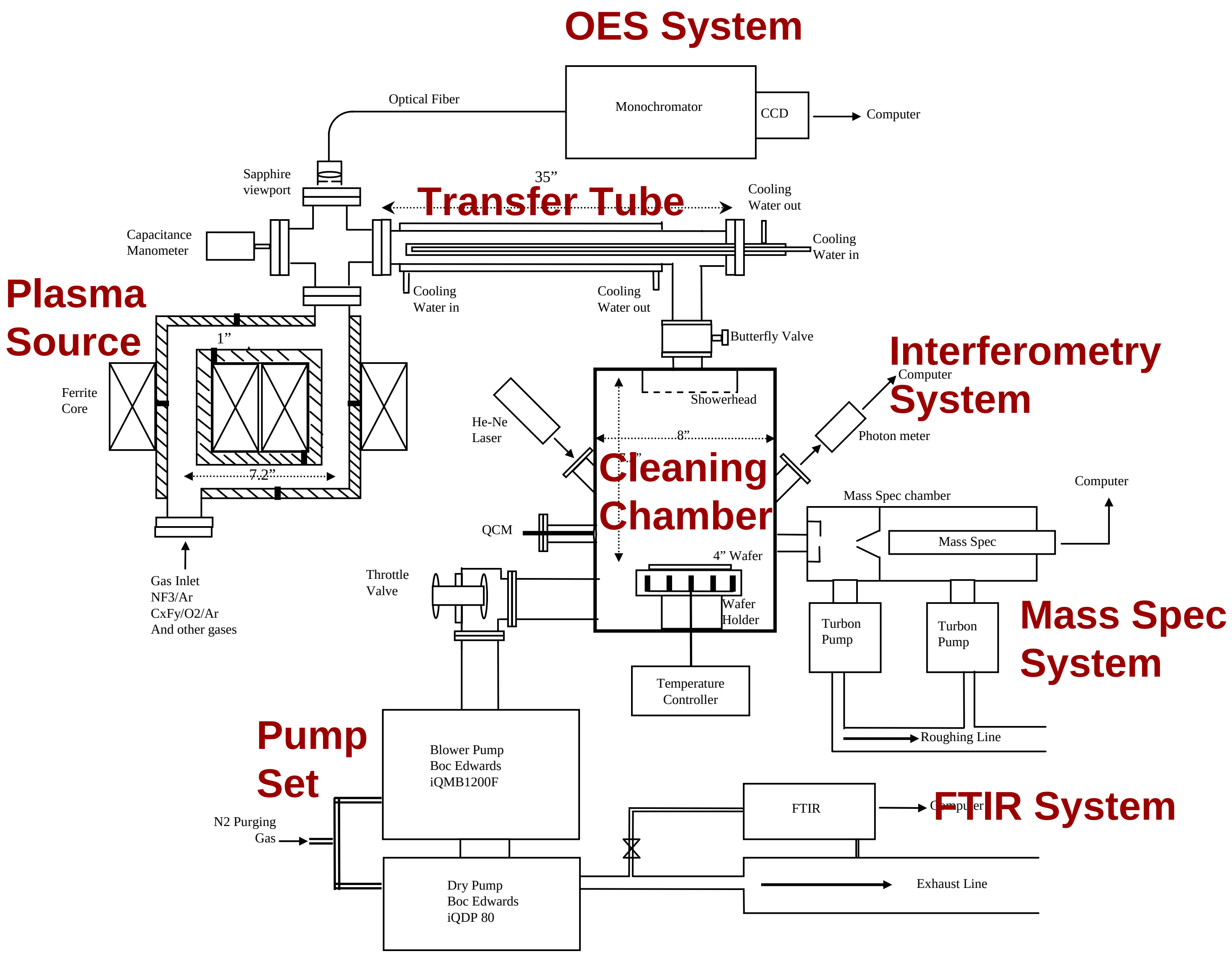
Remote Chamber Cleaning



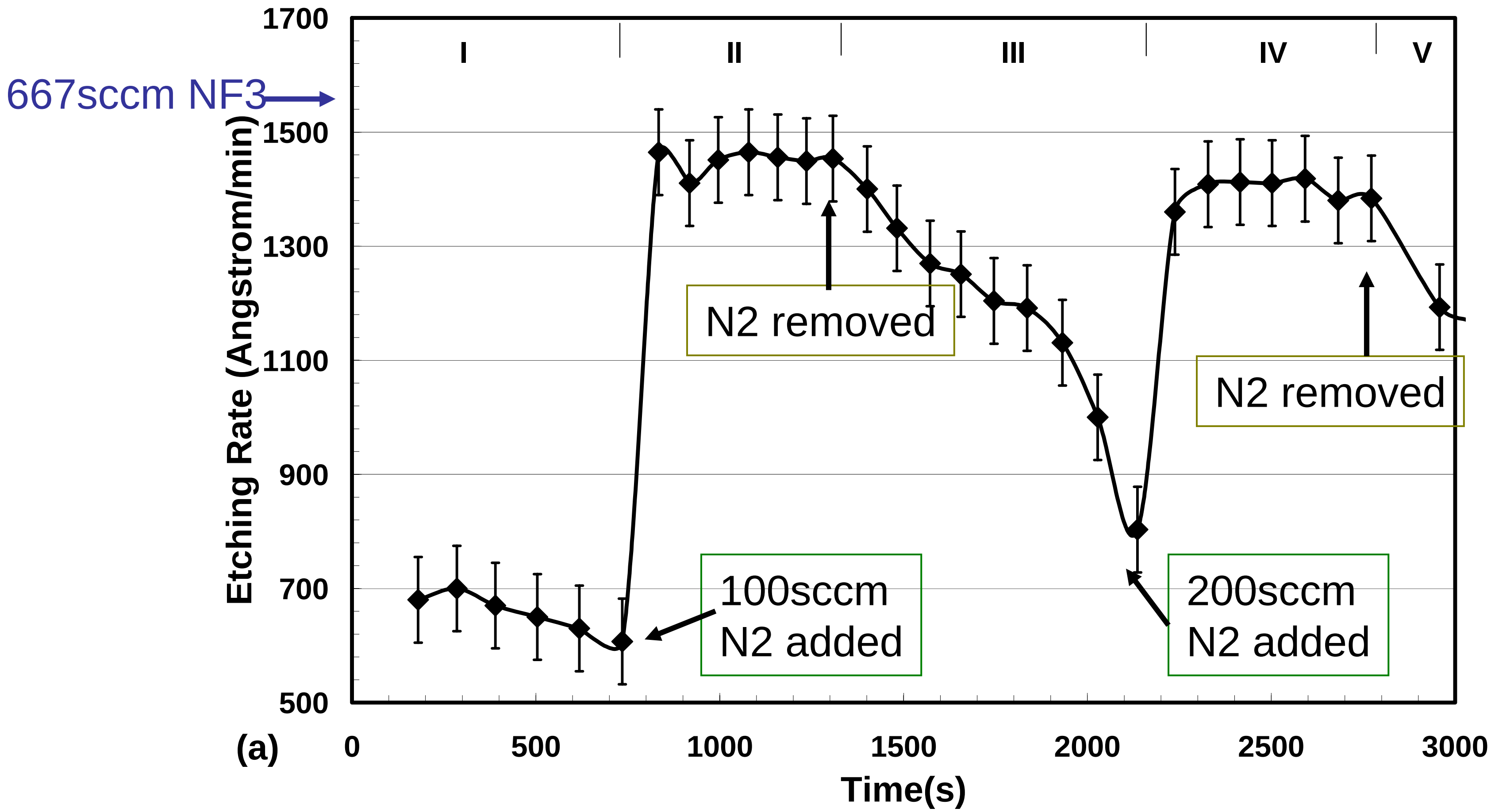
400kHz
ASTRON made by MKS ASTEX
Power → 14kW
Power Density → 40W/cm^3

- [illegible] temperature, electron temperature.

Detailed Scheme of the Apparatus

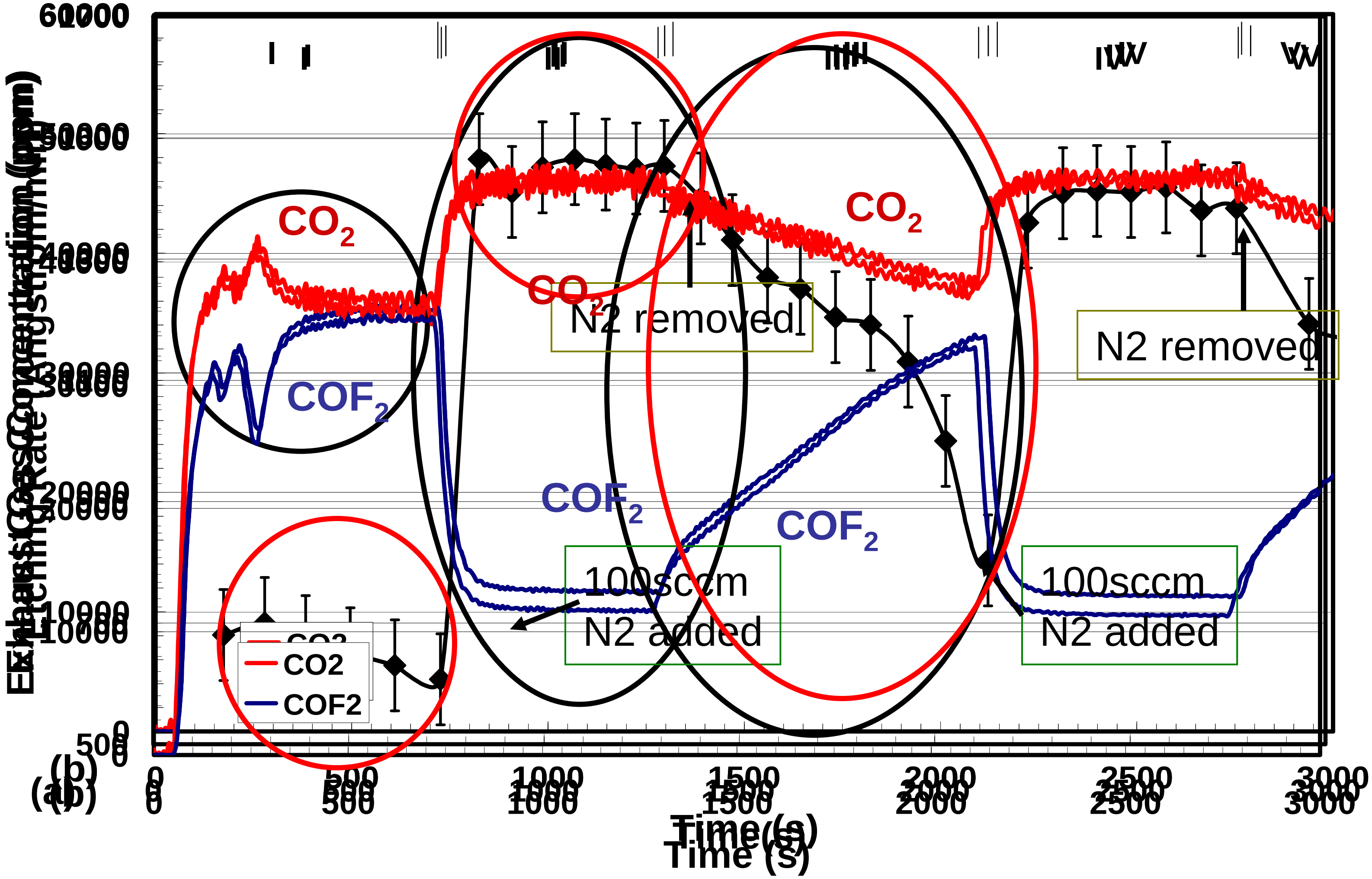


Effect of addition of N_2 in $C_4F_8+O_2+Ar$ plasmas



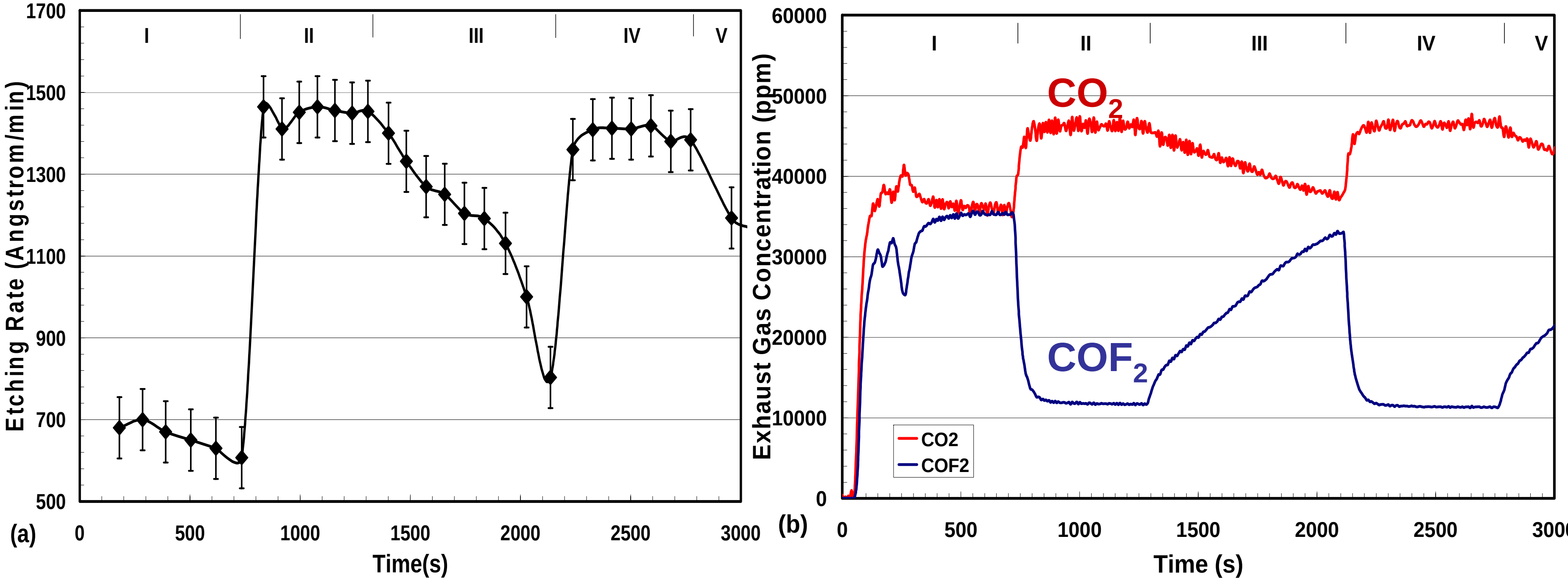
- Started at 250 sccm C_4F_8, 1750 sccm O_2 and 2000 sccm Ar
- Chamber pressure 2 torr, TEOS oxide film at 100^{o}C
- Under the same condition for 667 sccm NF_3, the etching rate is 1550A/min

Etching Rate Results vs FTIR



- Relaxation time 5 orders of magnitude longer than residence time
- Suggests a surface modification

FTIR Measurements v.s. Etching Rate



- Why is etching rate with C_xF_y is smaller than NF_3
  - Loss of F to COF_2 formation
- Why does N_2 addition improve etching rate with CxFy
  - Reduced COF_2 formation

- **How does addition of N_2 can reduce concentration of COF_2?**
  - **Due to the changes in the plasmas?**
  - **Due to downstream surface?**

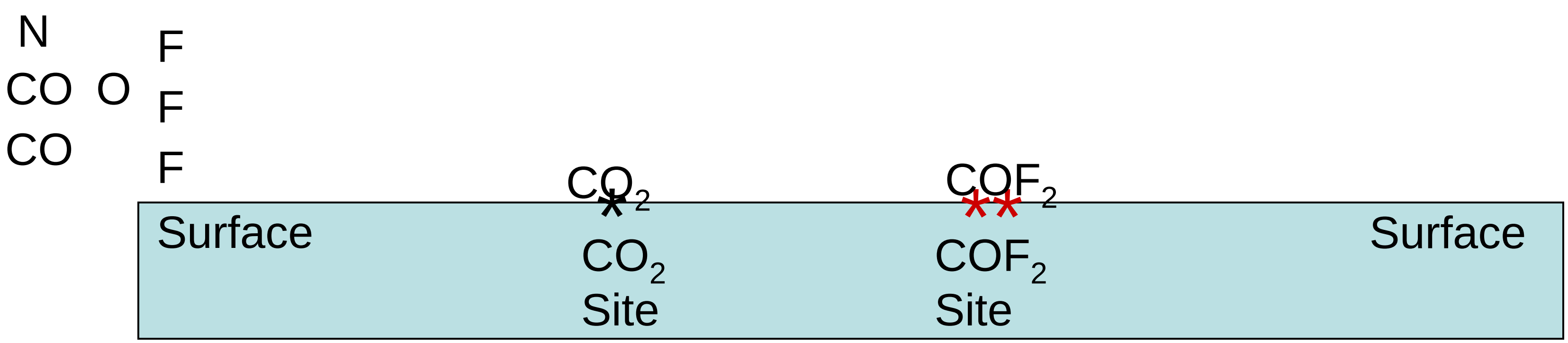
Maybe not because of the plasma source!

- No observable change of plasma physics, with addition of N_2:
  - Current and voltage waveform.
  - Spatial distribution of F and O atom concentration
  - Spatial distribution of neutral temperature
  - Spatial distribution of electron temperature
- The long lived effects and slow decay strongly suggest they are due to surface modification.

Proposed surface modification mechanism

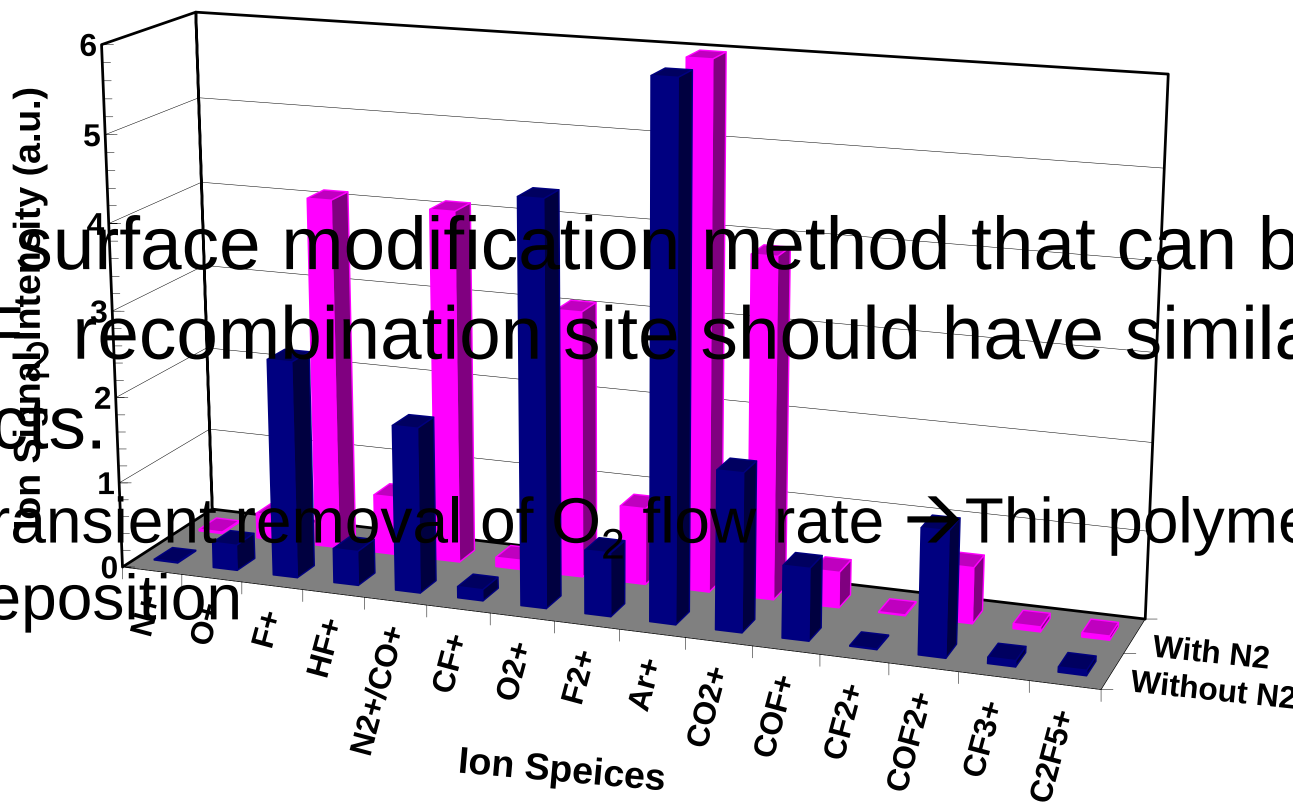
~~$CO + 2F + * \rightarrow COF_2 + *$~~

$$CO + O + ** \rightarrow CO_2 + **$$



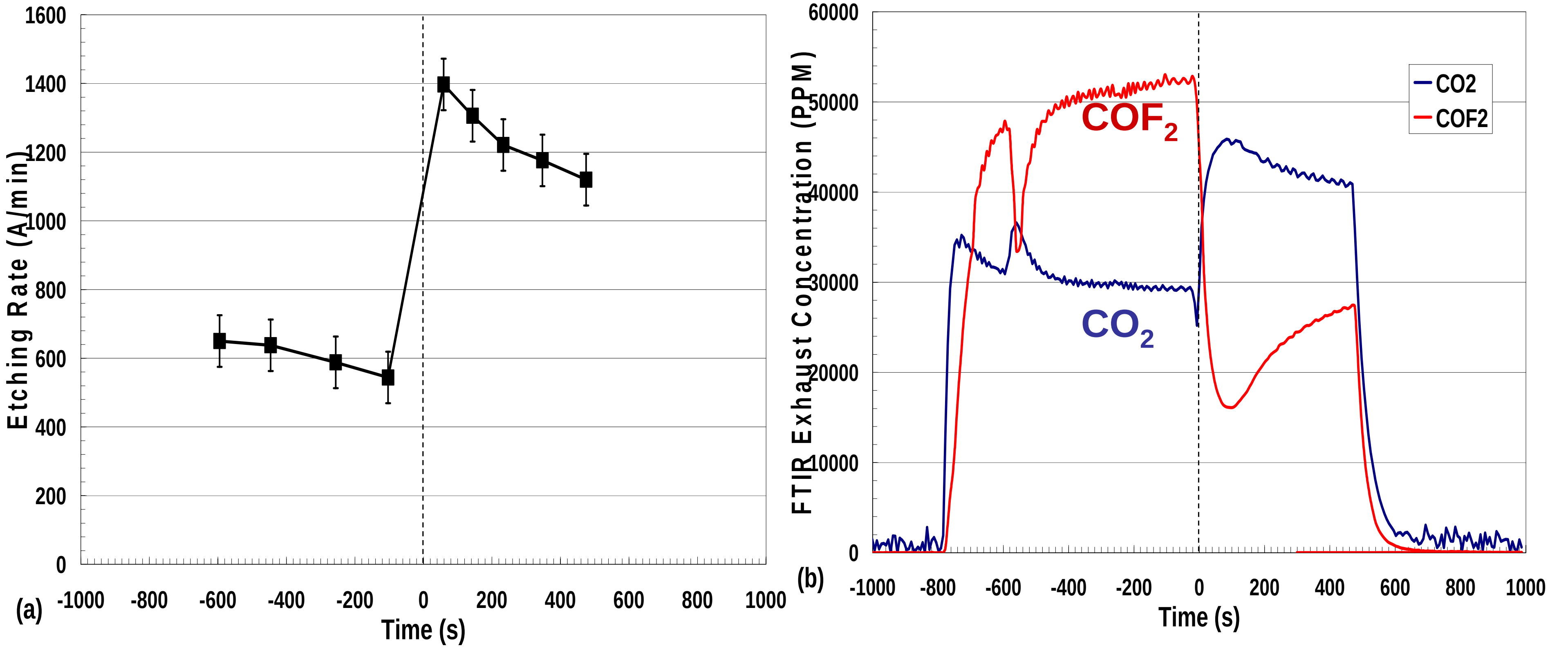
Confirmation by Mass Spectrometer

- The enhancement of etching rate by adding N_2 was observed for CF_4, C_2F_6, C_3F_8, C_4F_8.
- The enhancement of etching rate was observed for other N-containing gases like NO, NF_3 etc.
- Line-of-Sight Mass Spec for Condition: 667 sccm C_2F_6+333 sccm O_2+2000 sccm Ar



- Any surface modification method that can block COF_2 recombination site should have similar effects.
  - Transient removal of O_2 flow rate → Thin polymer deposition

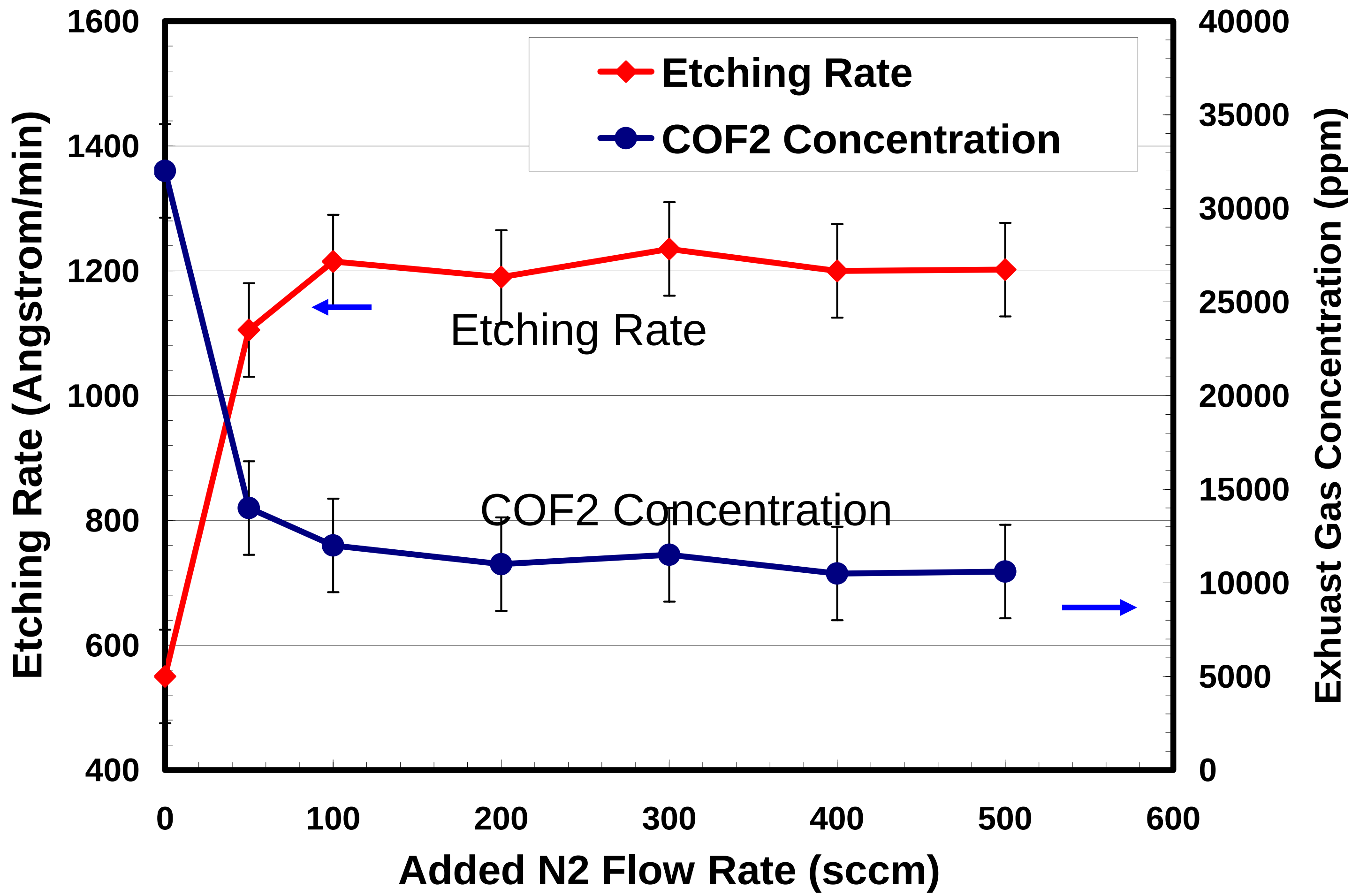
Transient removal of O_2 flow rate



•Condition: 250 sccm C_4F_8, 1750 sccm O_2 and 2000 sccm Ar
•The method is not preferred due to polymer deposition

Saturation of N_2 addition

- For surface site blocking, more N_2 addition shouldn't further increase the etching rate.



Summary

- For remote chamber cleaning, C_2F_6 can have comparable performance as NF_3 for the same flow rate of elemental fluorine.
- COF_2 is the key to determine the cleaning performance of fluorocarbon gases.

$$\sout{CO + 2F + * \rightarrow COF_2 + *}$$

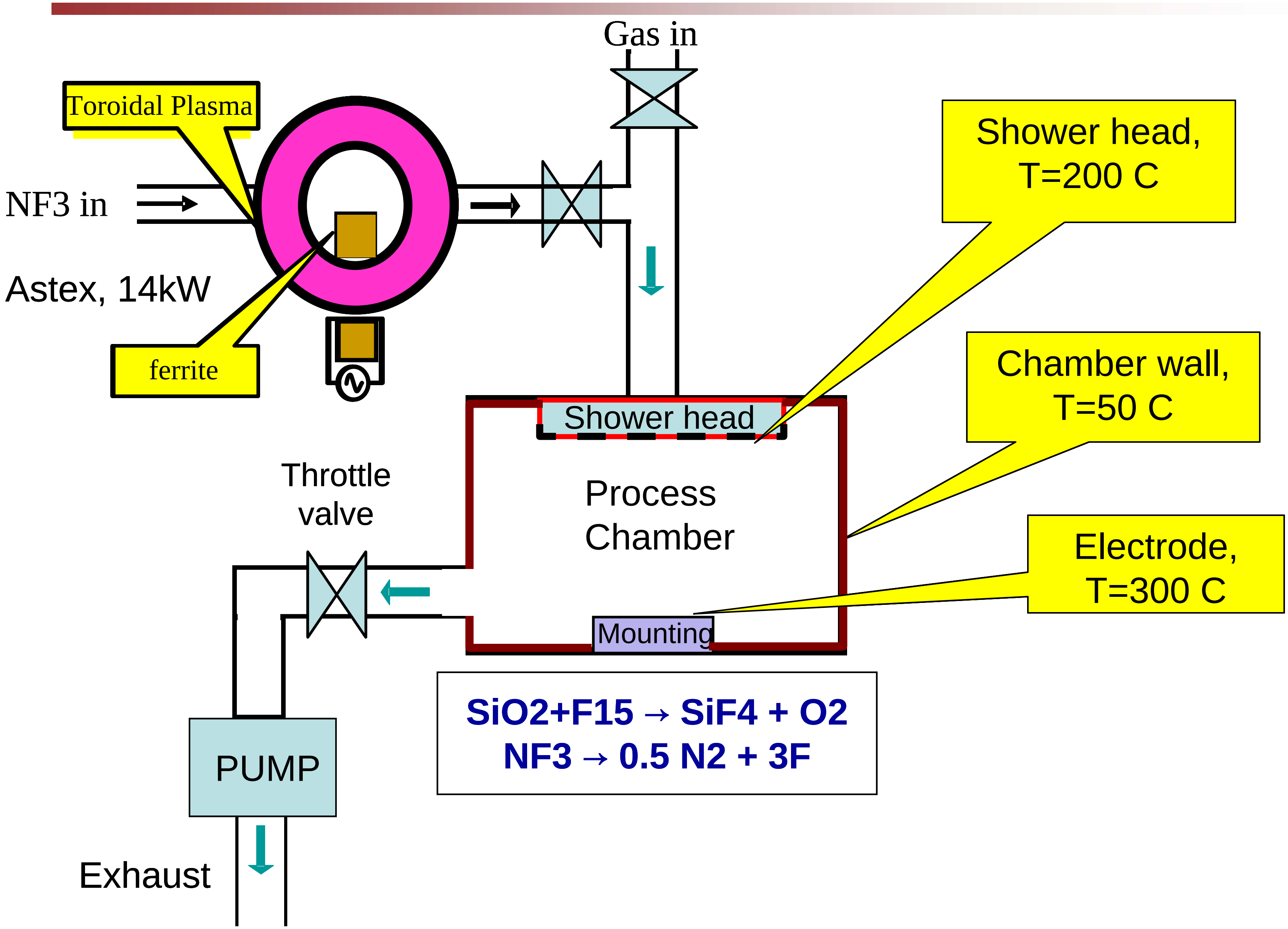
N atoms

$$CO + O + ** \rightarrow CO_2 + **$$

More F atoms

Saturation of Etching Rate in Downstream Plasma Chamber Cleaning

PECVD Chamber Cleaning



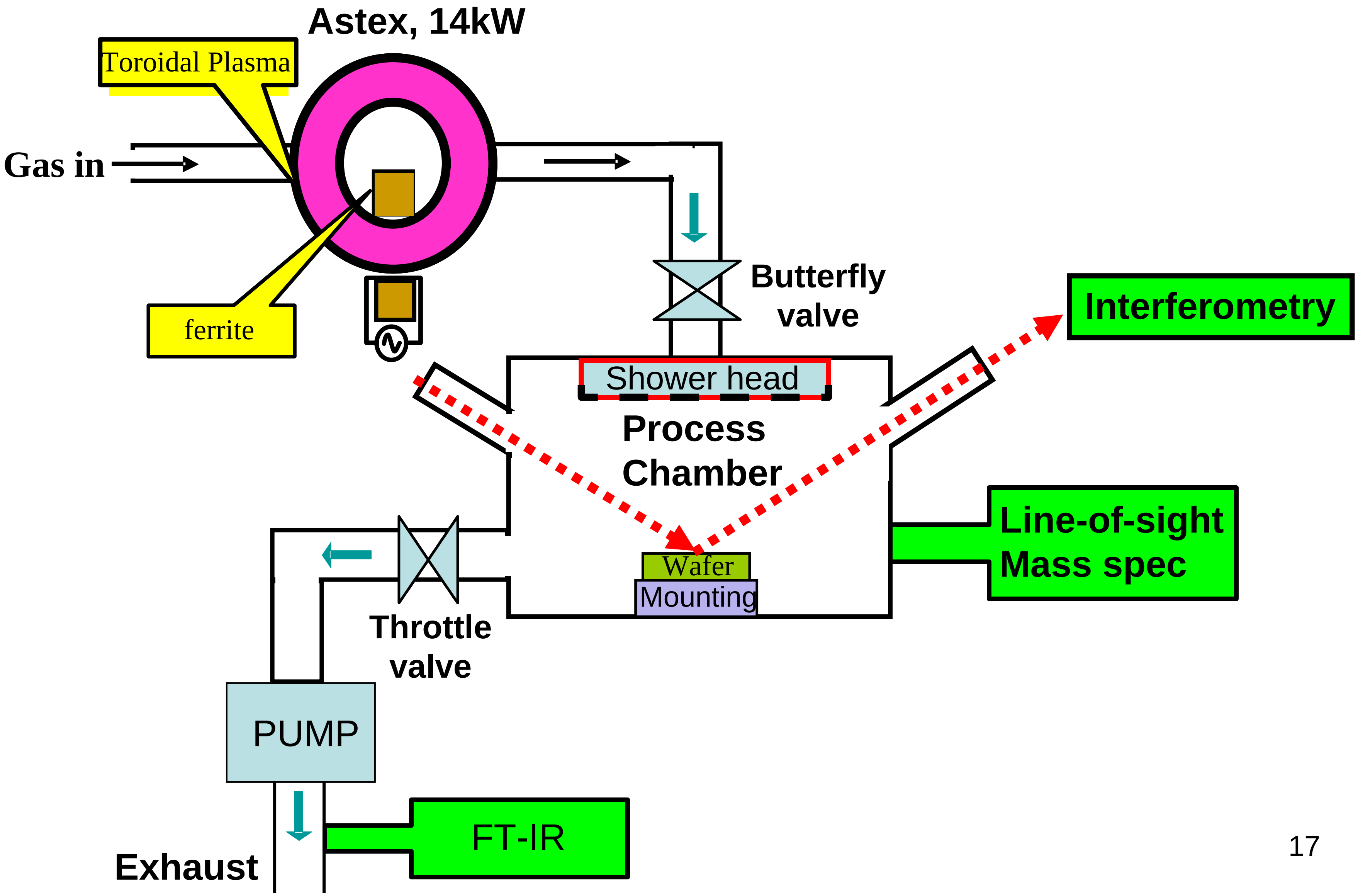
$SiO_2 + F_{15} \rightarrow SiF_4 + O_2$

$NF_3 \rightarrow 0.5\ N_2 + 3F$

Problem : Is Maximizing NF3 flow rate the best way to clean PECVD chamber?

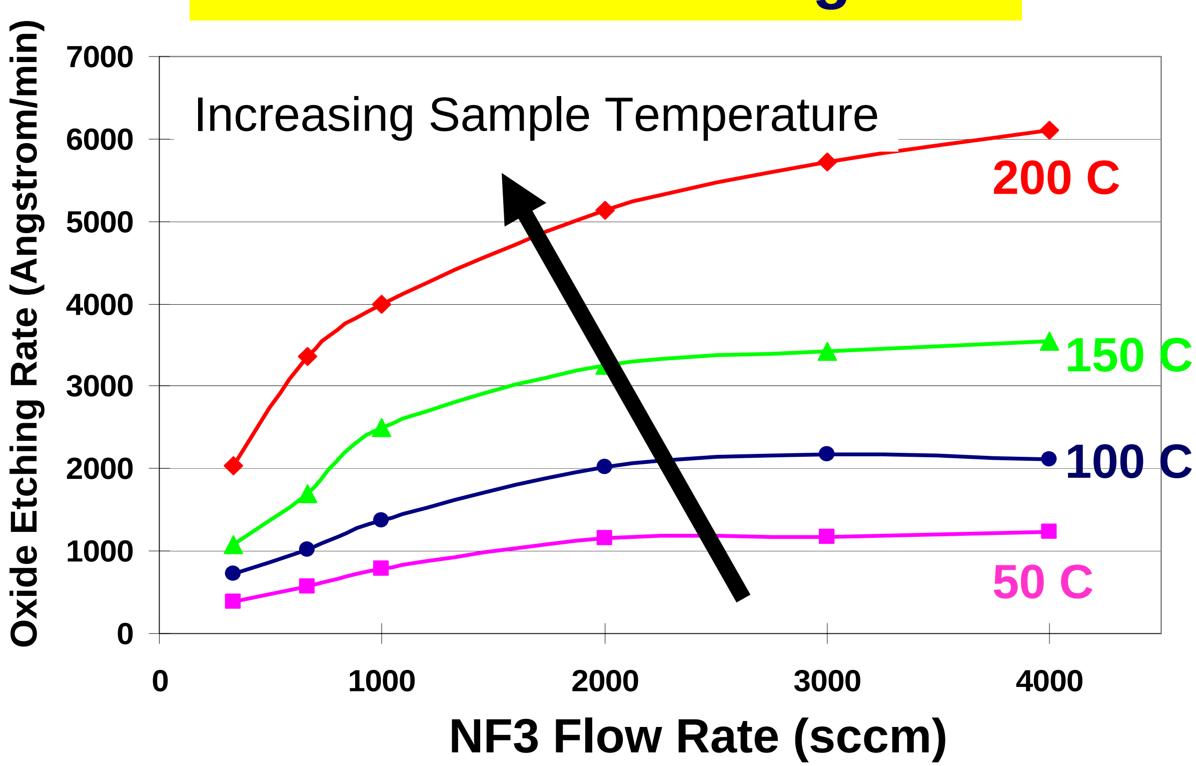
- Time to clean PECVD Chamber
  - Three different temperature and cleaning area
    - Chamber Wall (T=50 C)
    - Shower head (T=200 C)
    - Electrode (T=300 C)
- Conventional Cleaning Operation
  - Maximize NF_3 Flow Rate
  - Maximize Pumping Rate to Exhaust
- Another approach : Kinetics
  - Adsorption limiting regime : Inlet NF_3 amount will affect etching rate
  - Reaction limiting regime : Inlet NF_3 amount will not affect etching rate

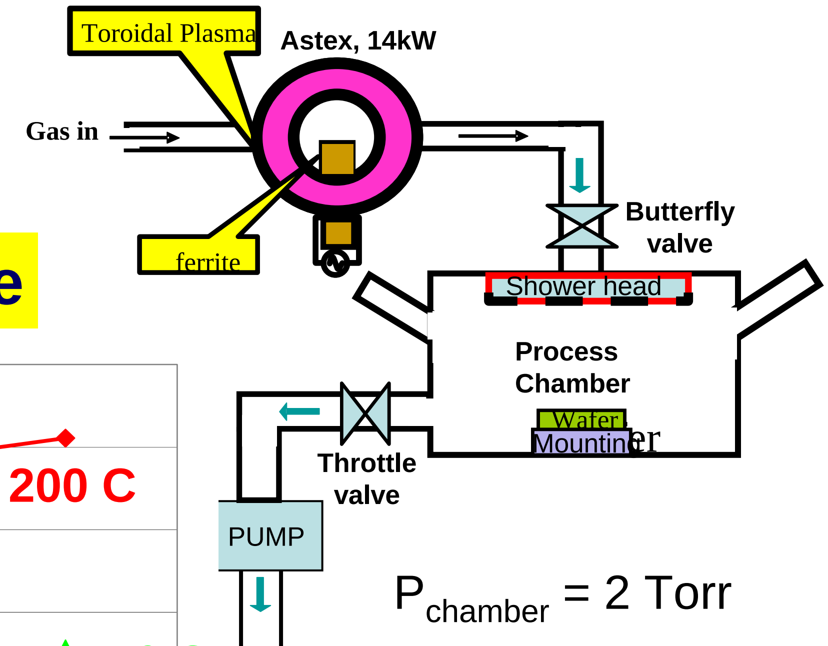
Experimental Apparatus



Etching Rate vs NF3 Flow Rate

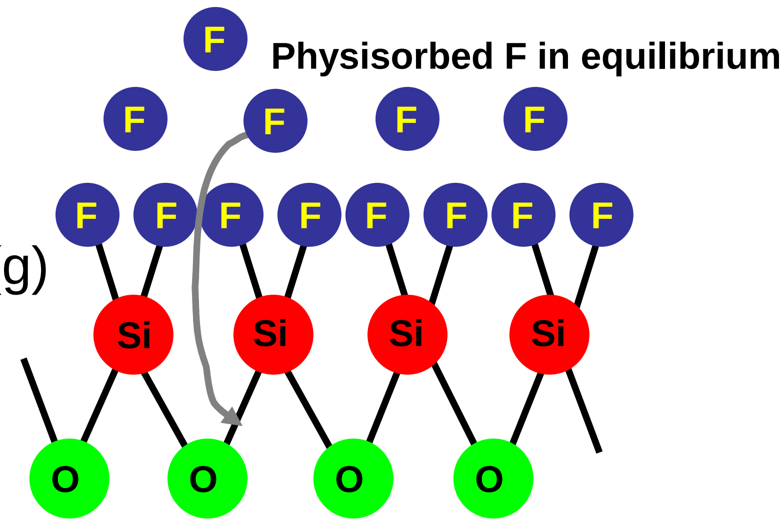
Saturation of Etching Rate





Langmuir-Hinshelwood Kinetics

- Physisorption
  - F(g) $\leftrightarrow$ F(ads)
- Surface Reaction
  - $4F(ads) + SiO_2(solid) \rightarrow SiF_4(g) + O_2(g)$



- Two regimes:
  - Linear regime: If P_F is small, the etching rate is linearly dependent on partial pressure of fluorine. The temperature dependence is Arrenhius-like.

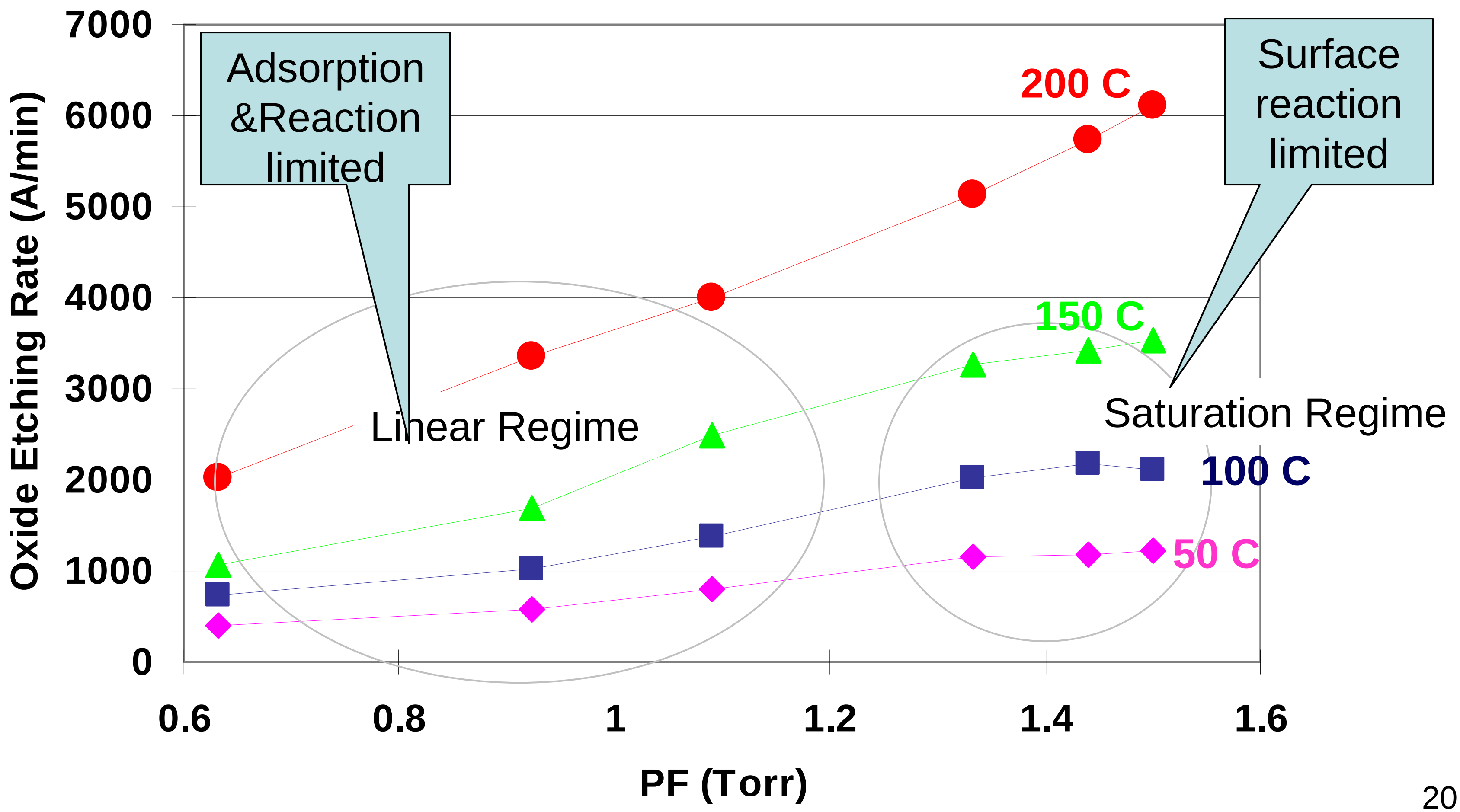
$$ER \propto \frac{1}{\sqrt{T}} P_F \cdot e^{-\frac{(E_{reaction} - E_{desorption})}{RT}}$$

  - Saturation regime: If P_F is large, the etching rate is independent of partial pressure of fluorine.

$$ER \propto e^{-\frac{E_{reaction}}{RT}}$$

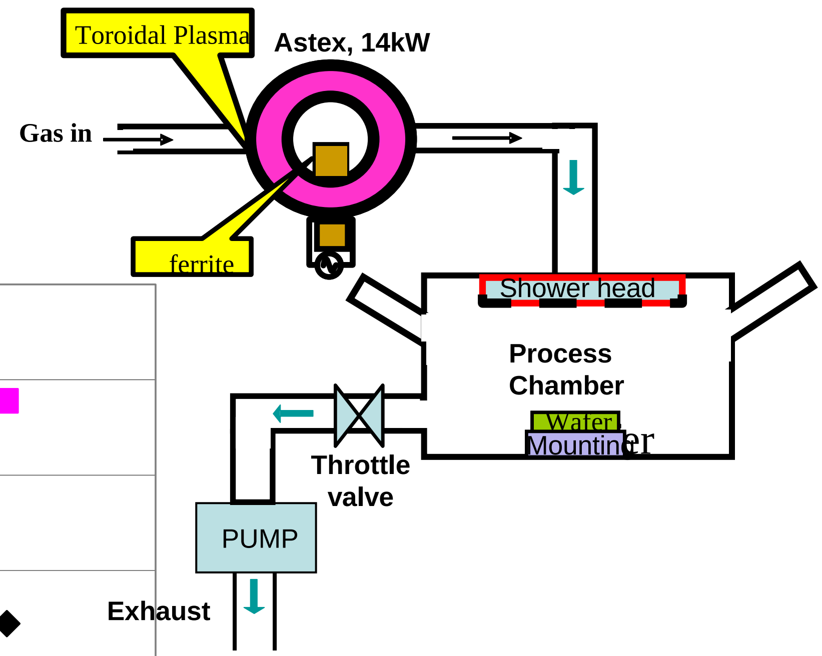
Etching rate vs F partial pressure

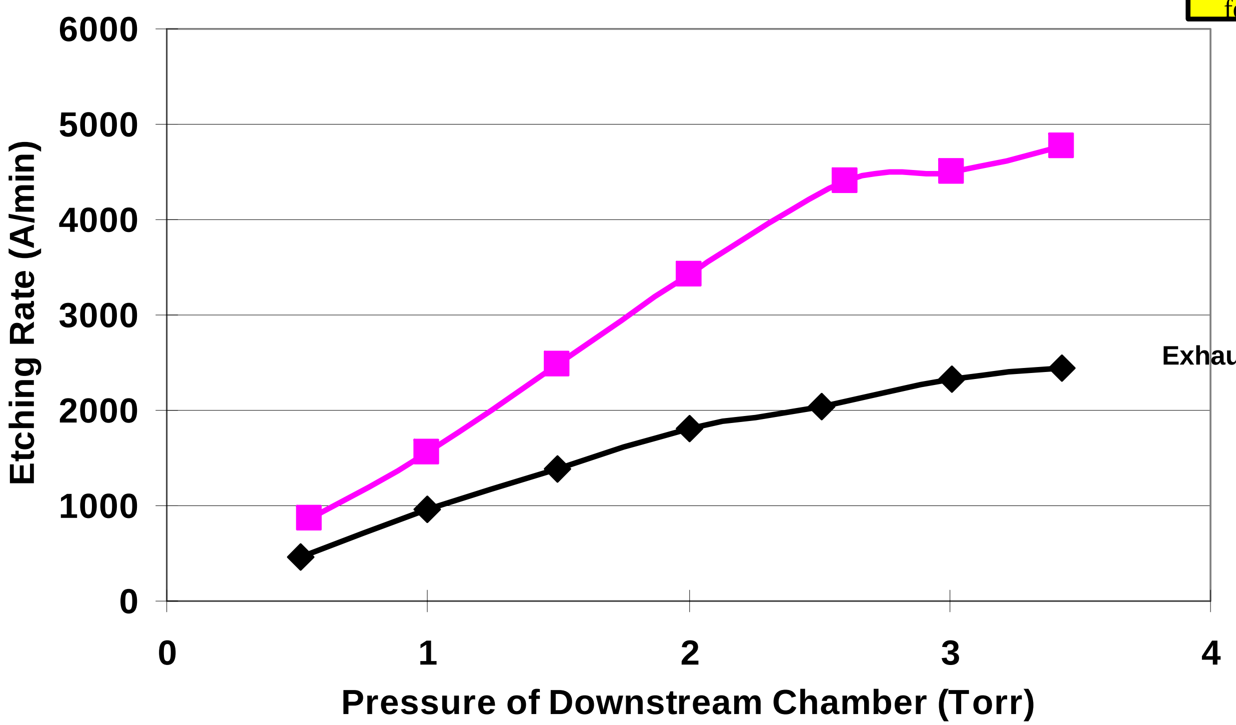
- Assuming complete dissociation of $NF_3 \rightarrow 0.5N_2 + 3F$



Confirmation experiments

- To confirm above observation, we fixed the pressure of the plasma source (4 torr) and independently changed the process chamber pressure.
- Similar saturation was observed
  (2000Ar/2000NF3).





Maximum Etching Rate and Threshold Fluorine Concentration

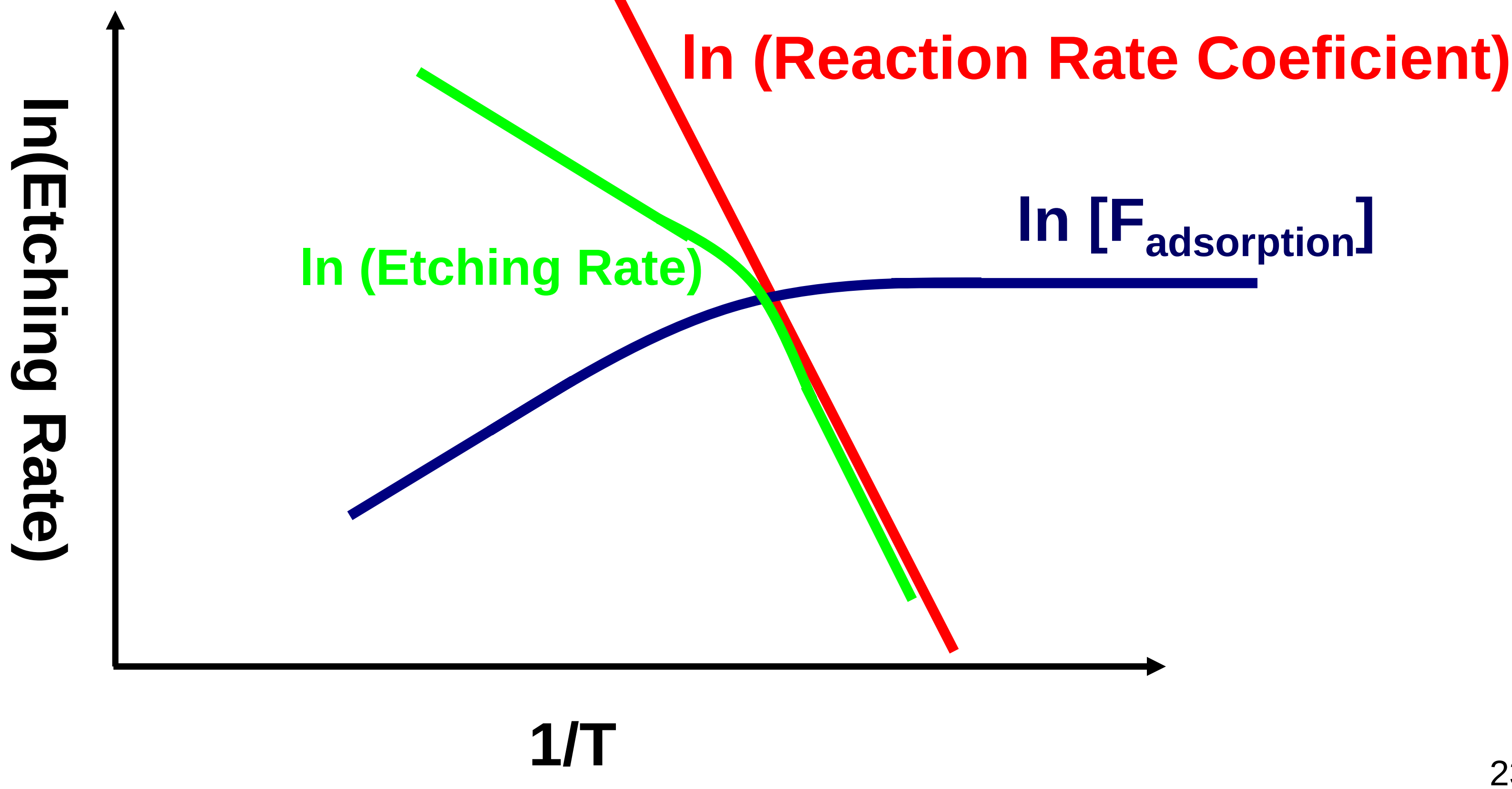
Wafer Temperature	Saturation Etching Rate	Threshold partial pressure of Fluorine
^{o}C	A/min	torr
50	1230	~1.4
100	2100	~ 1.6
150	3600	~ 1.8
200	7000-8000	~ 2.2

- Calculation of the threshold atomic fluorine concentration:
  - Using the experimentally measured temperature in the source
  - Using the experimentally measured pressure in the source and in the cleaning chamber
  - Using the measured atomic fluorine concentration in the plasma source

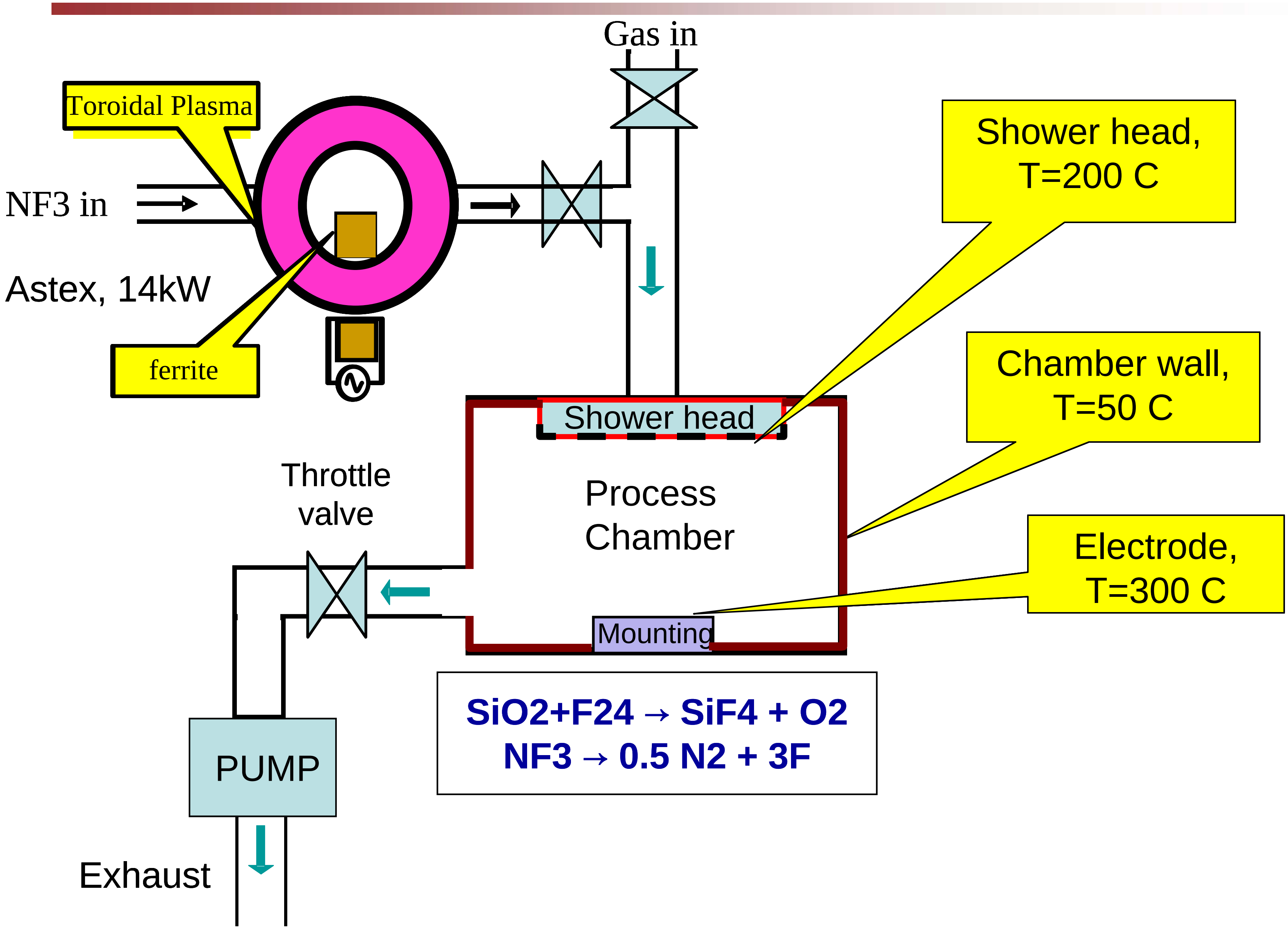
Change of saturation threshold

$$Etching\_Rate \propto [F_{adsorption}] \times \exp(-\frac{E_{reaction}}{RT})$$

Saturation Threshold Change



PECVD Chamber Cleaning



$SiO_2 + F_{24} \rightarrow SiF_4 + O_2$

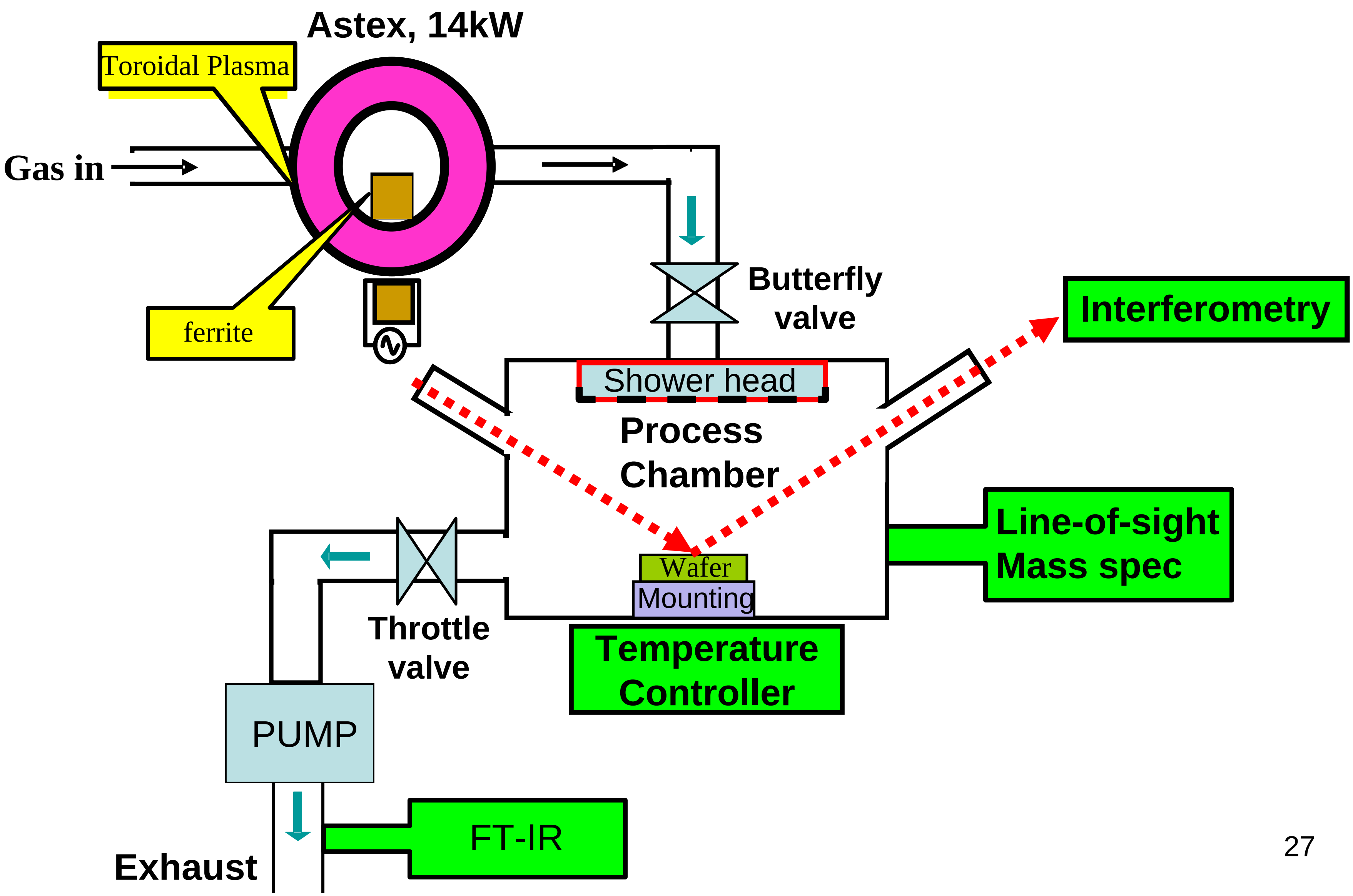
$NF_3 \rightarrow 0.5\ N_2 + 3F$

Summary

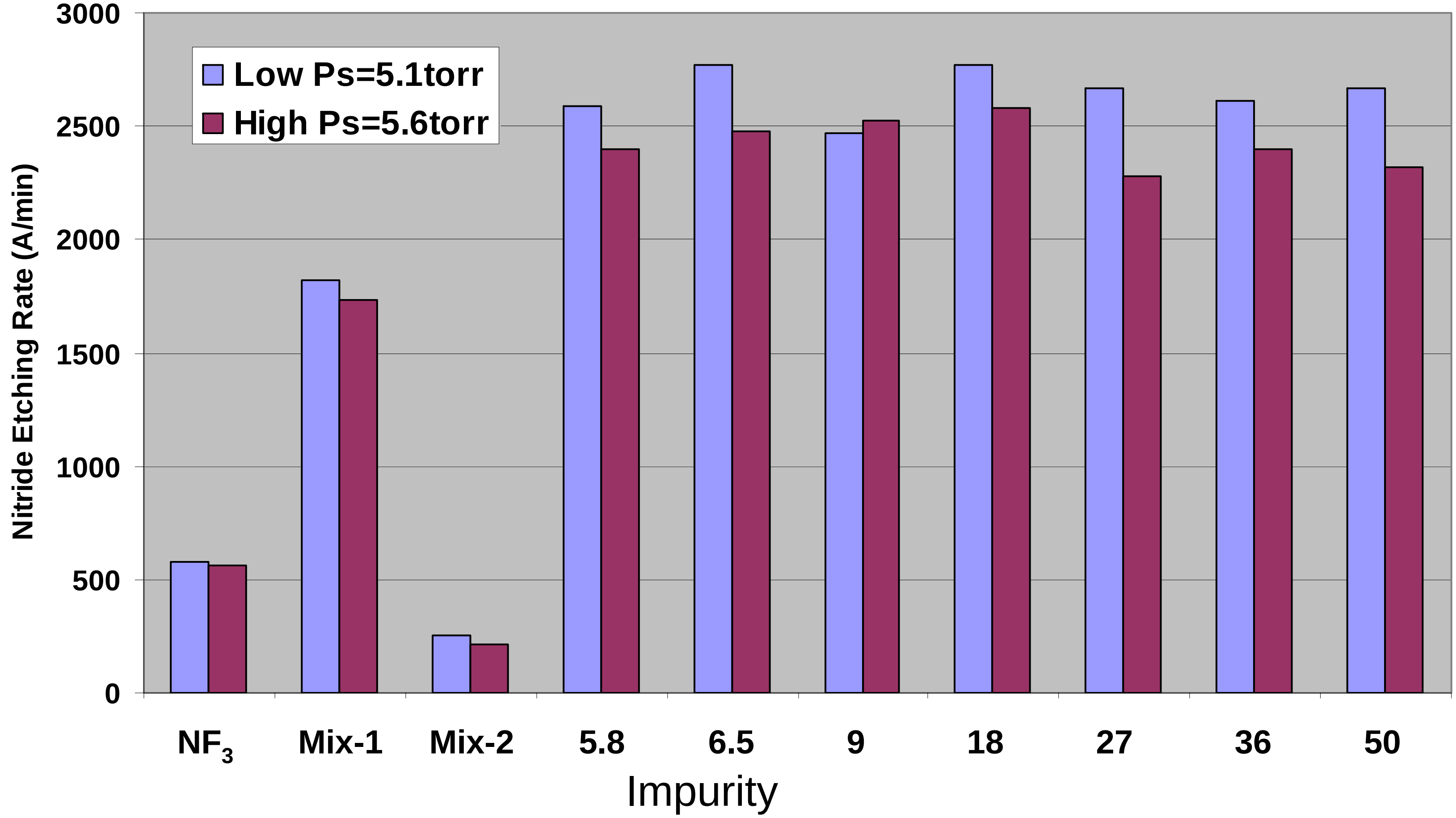
- Saturation of Oxide Etching Rate
  - P_F small : Linear regime
  - P_F large : Saturation regime
- Saturation can be explained by Langmuir-Hinshelwood Mechanism
- Flamm(1979)'s Results introduced Linear Regime
- Optimum Condition for Chamber Cleaning
  - Linear regime : Increase NF_3 flow rate
  - Saturation regime : Increase temperature

Synergistic Effect of NF_3 vs. Gas Blend on Nitride Film

Experimental Apparatus

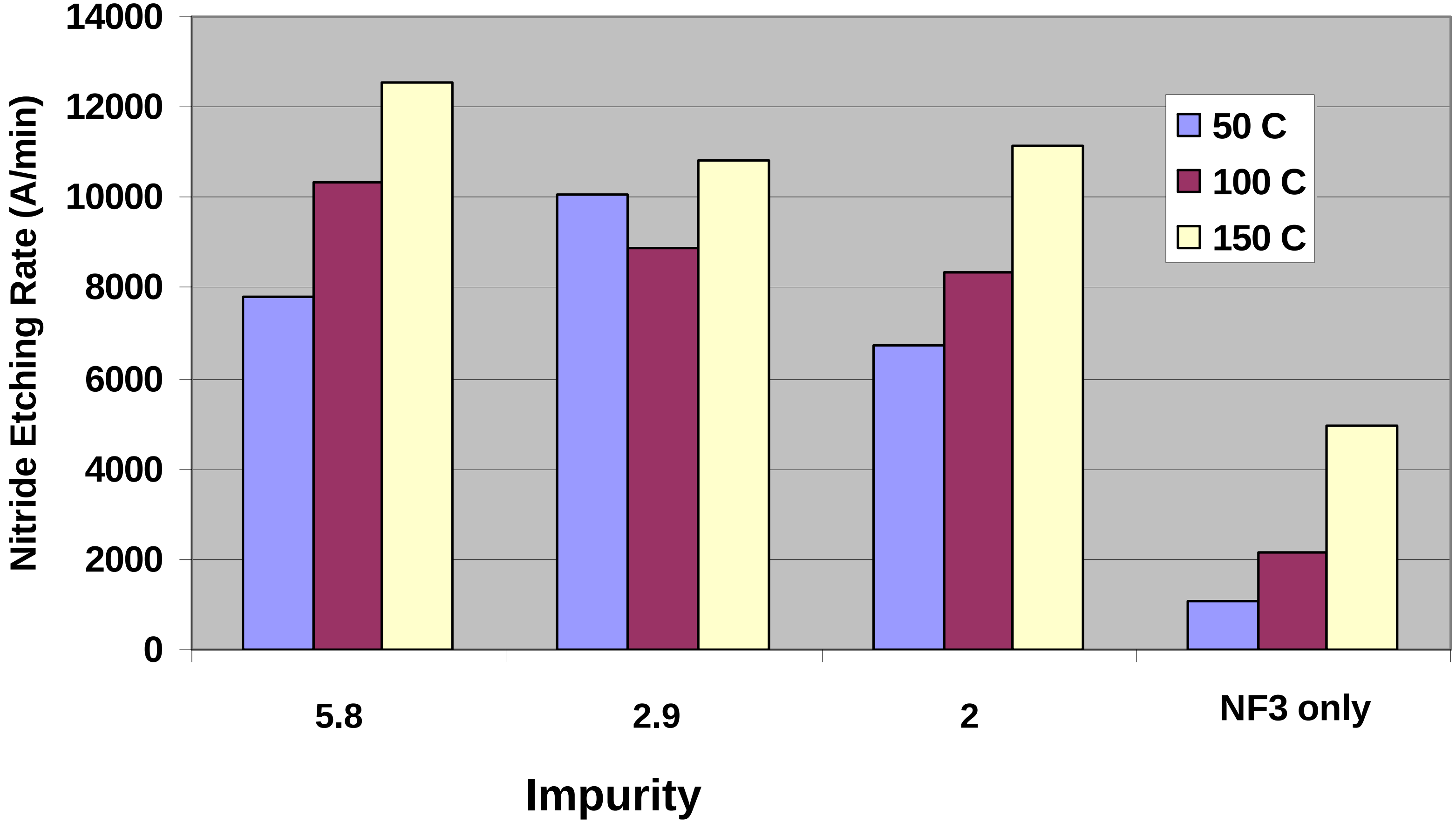


Enhancement of Etching Rate



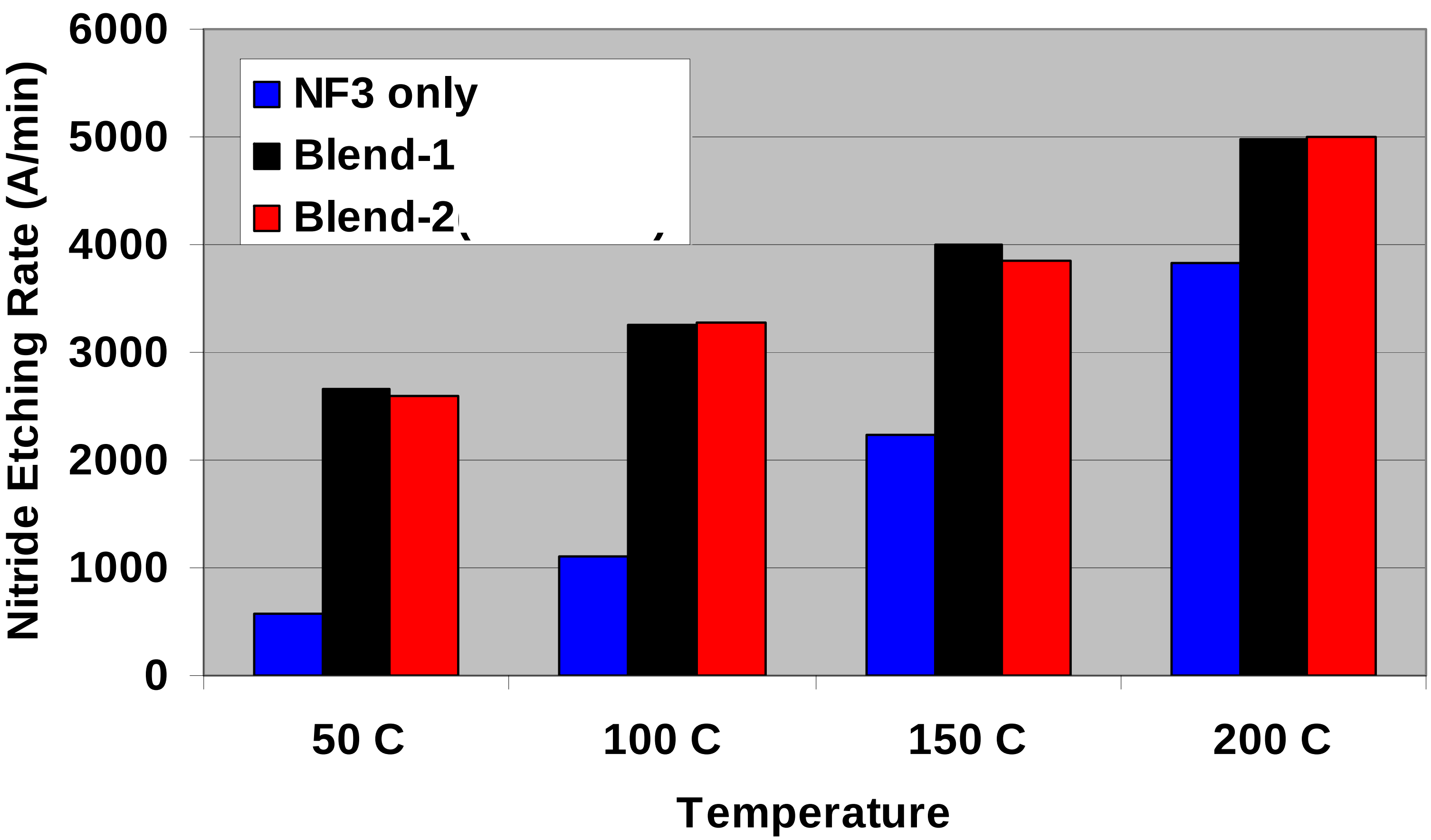
- $P_{chamber}$ = 5 torr, $T_{electrode}$ = 50 °C
- Etching Rate increases more than 4 times that of pure NF_3[28]

Impurity Level

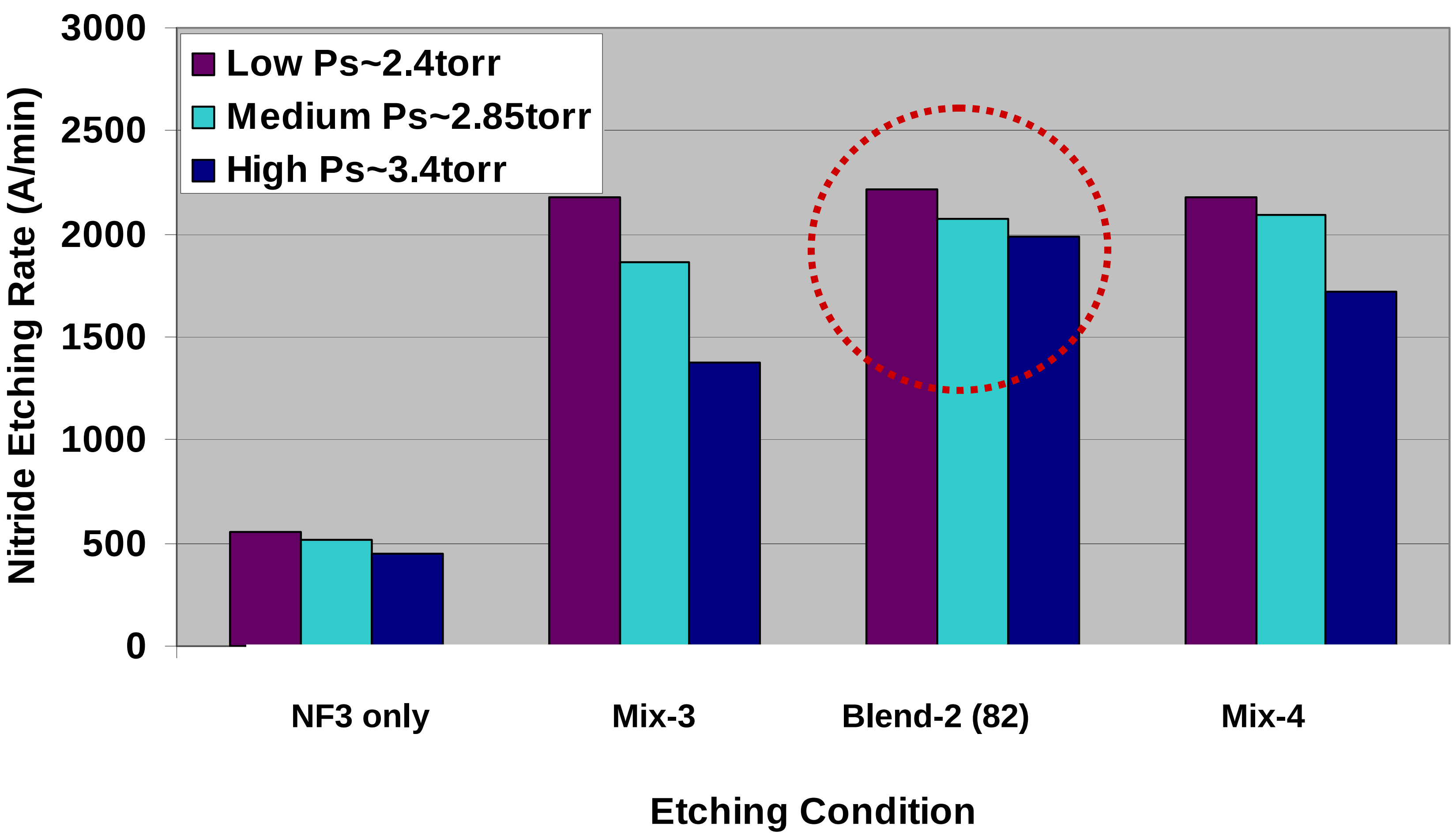


- Only 2% of addition can make 4x change
- Tflow = 4800 sccm, $P_{chamber}$ = 5 torr, P_{source} = 5.9 torr

Temperature Effect

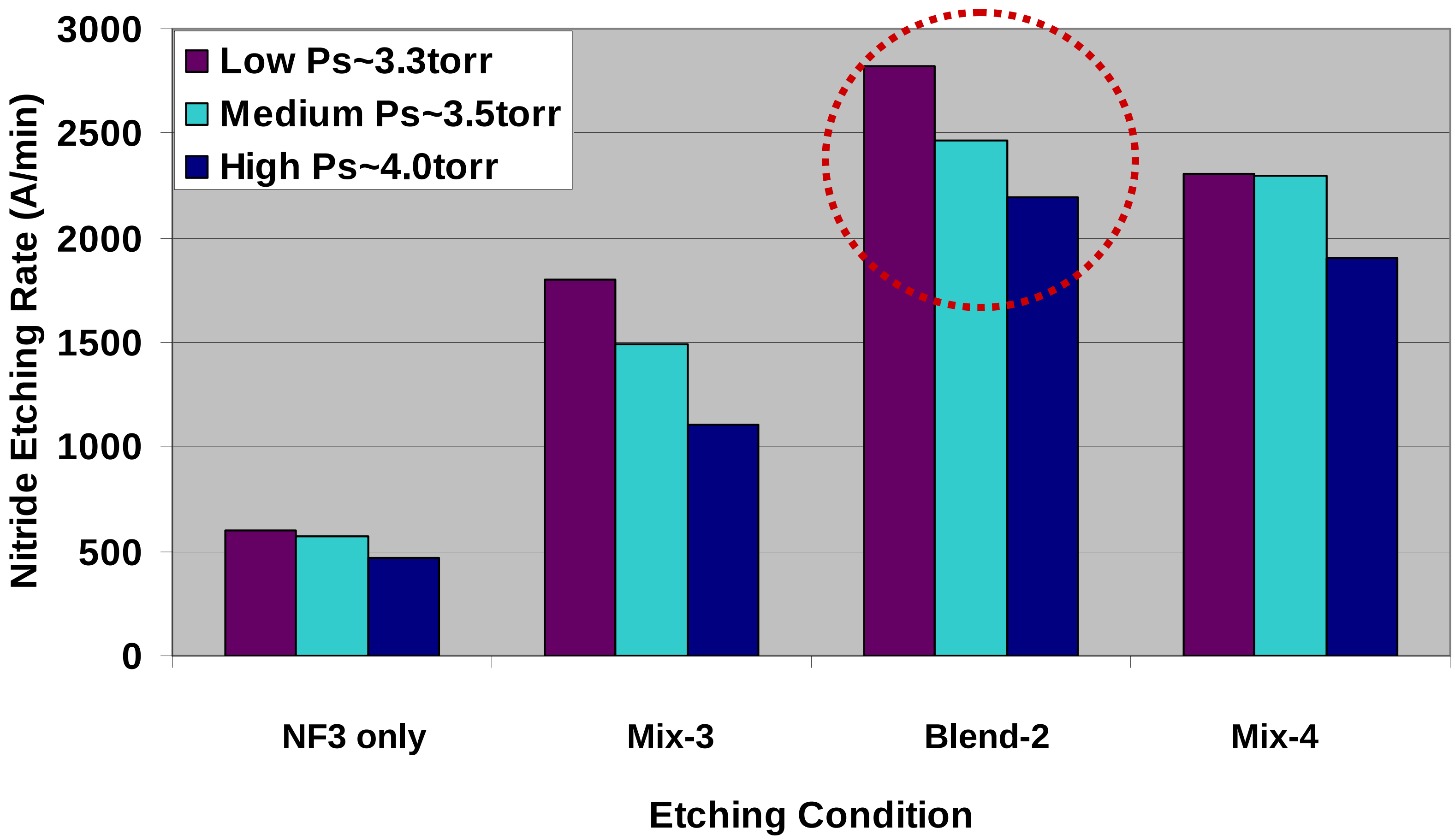


Nitride Film Etching @ Pc=2torr

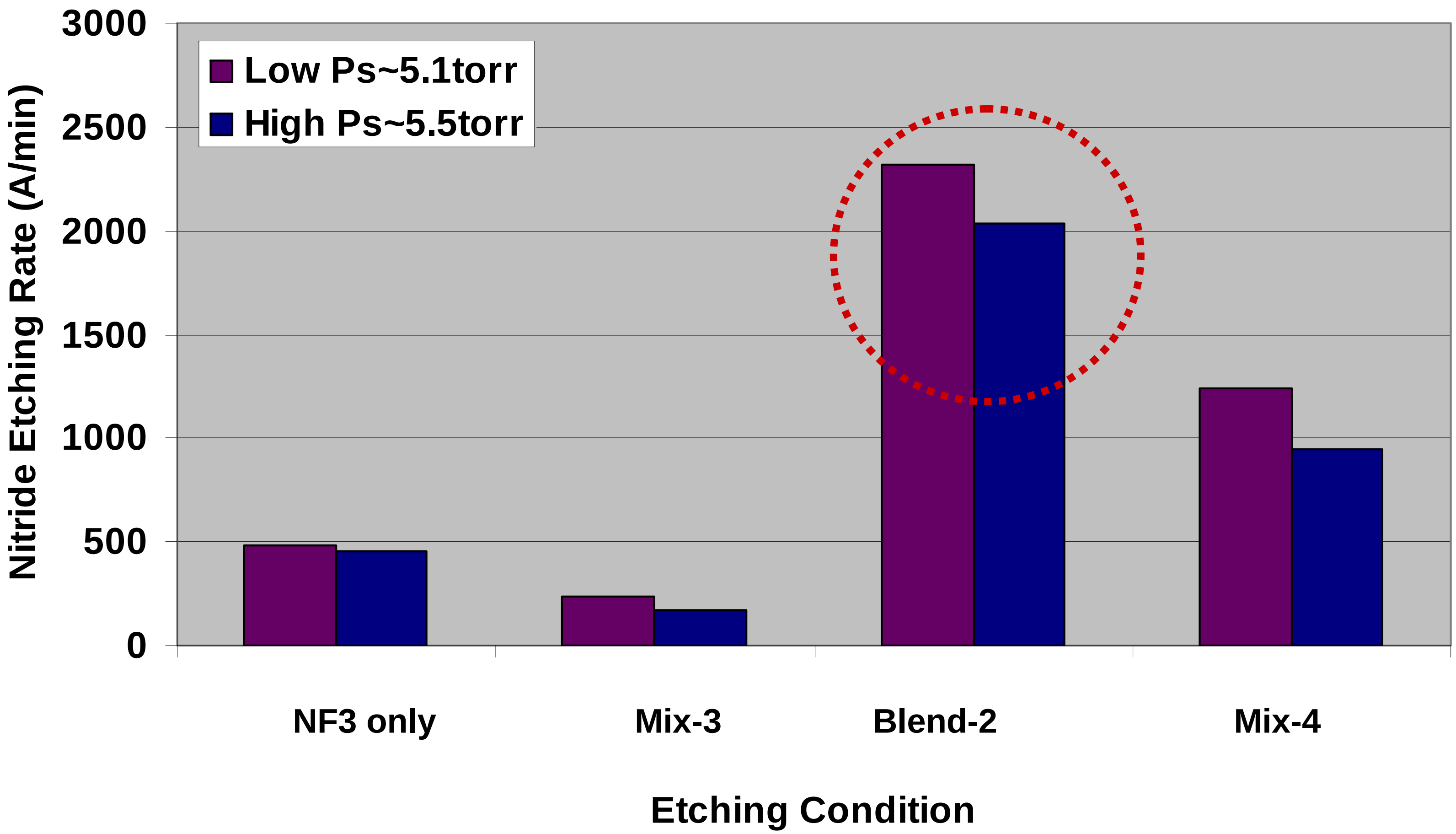


- Blend has advantage at higher chamber pressure

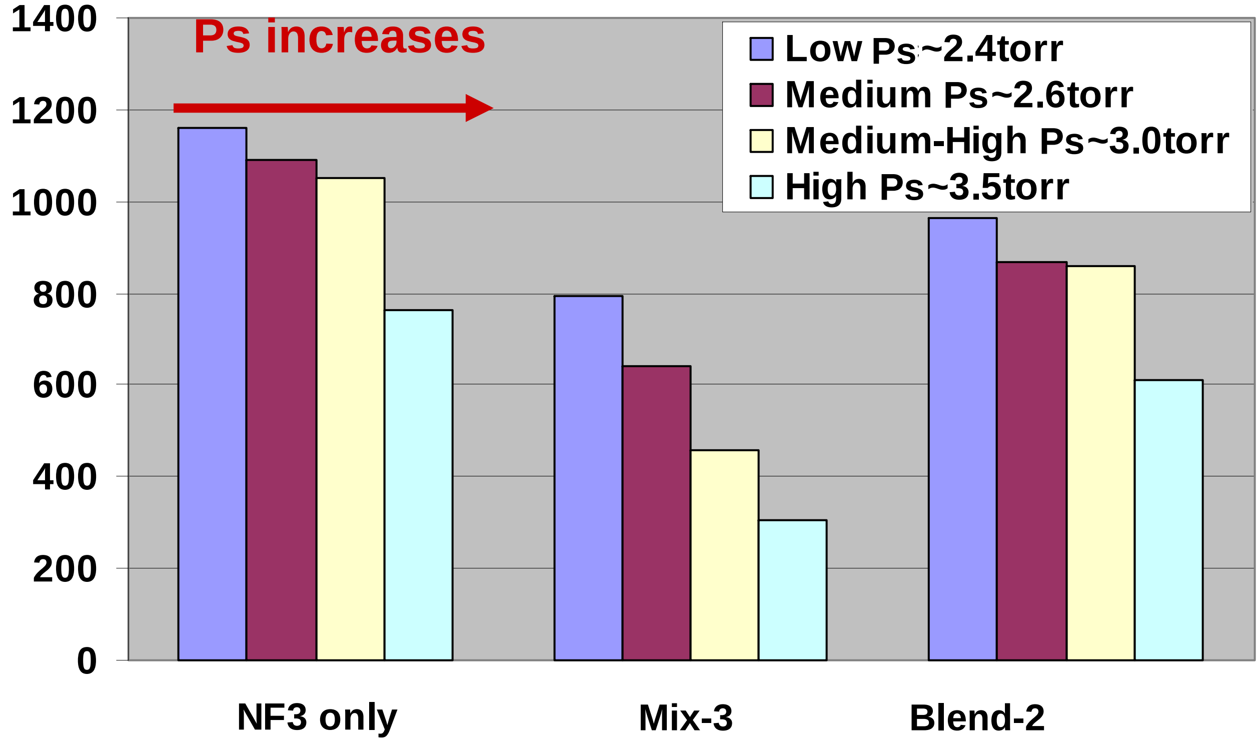
Nitride Film Etching @ Pc=3torr



Nitride Film Etching @ Pc=5torr

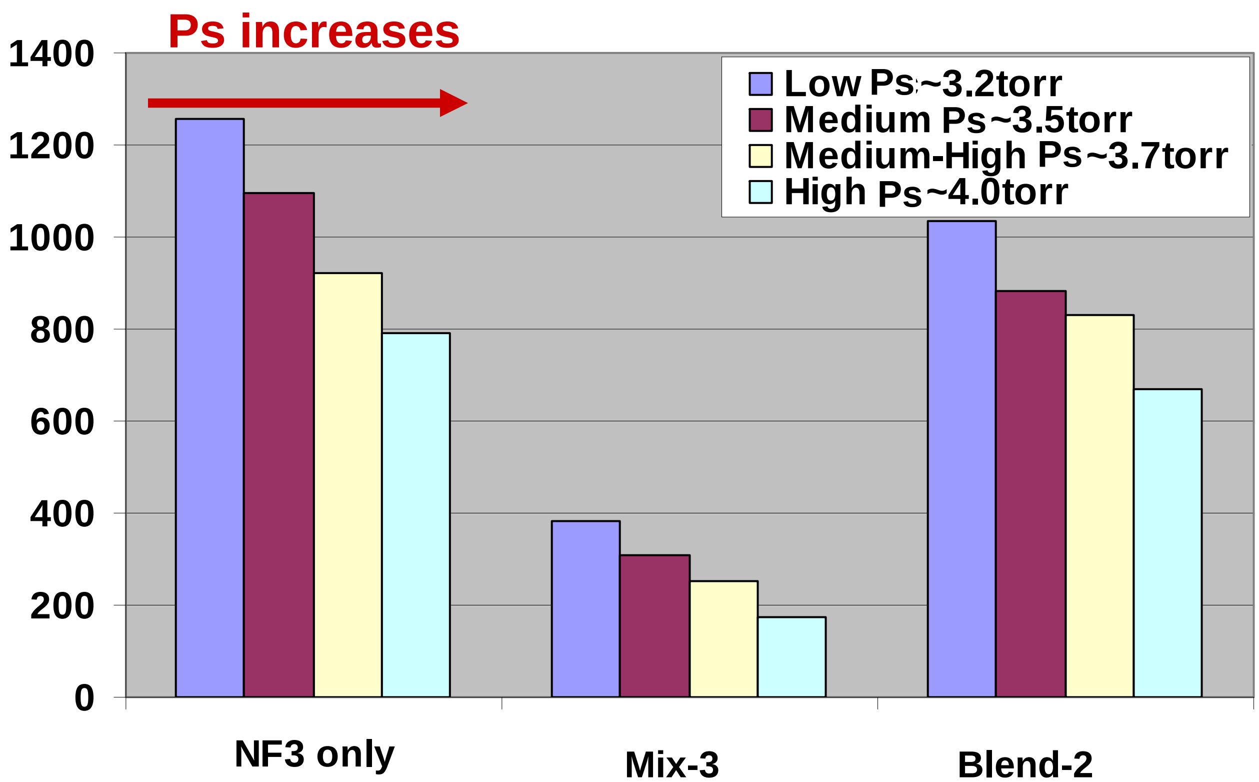


Oxide Film Etching @ Pc=2torr



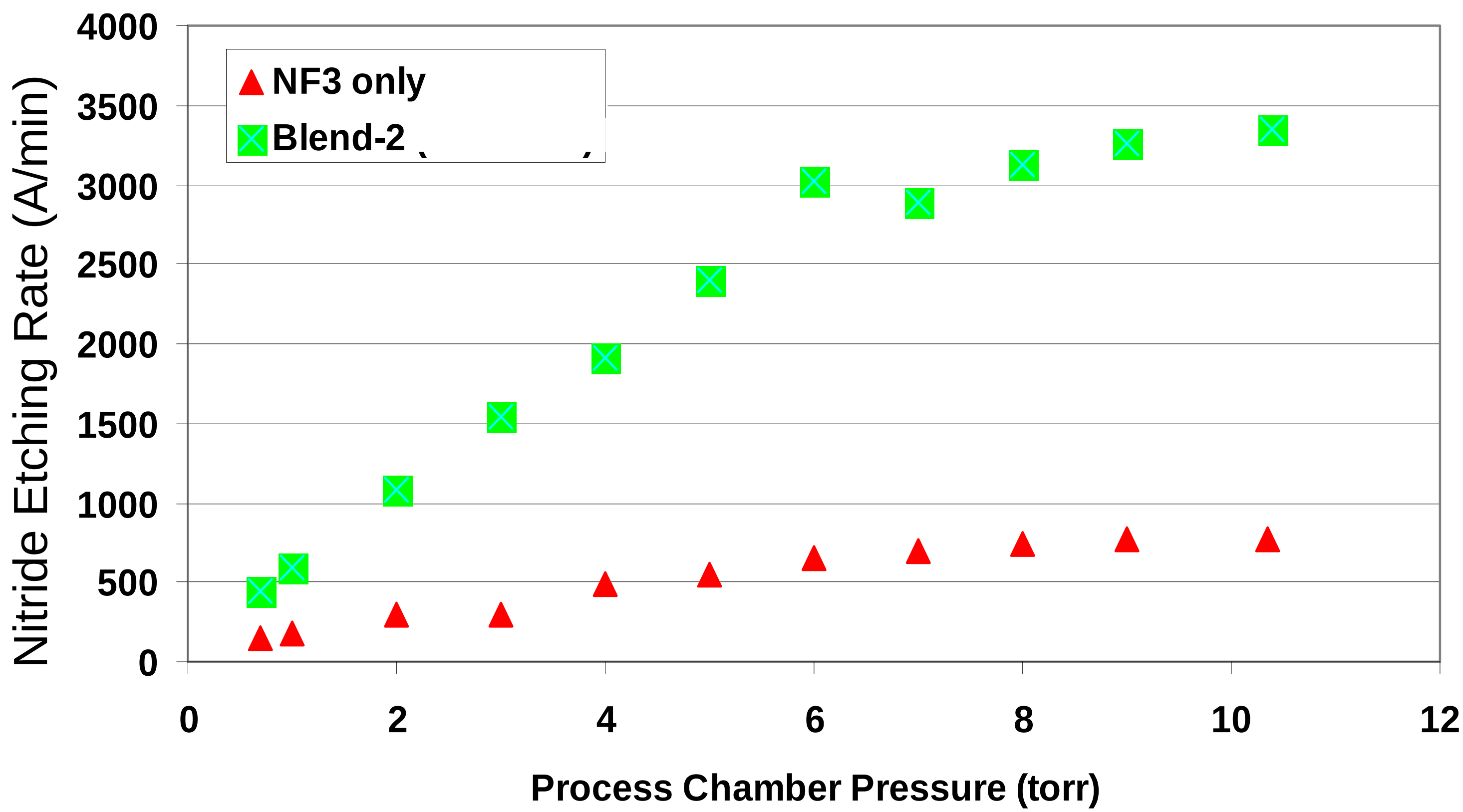
•**Blend-2 does not have advantage in etching rate on Oxide Film**

Oxide Film Etching @ Pc=3torr



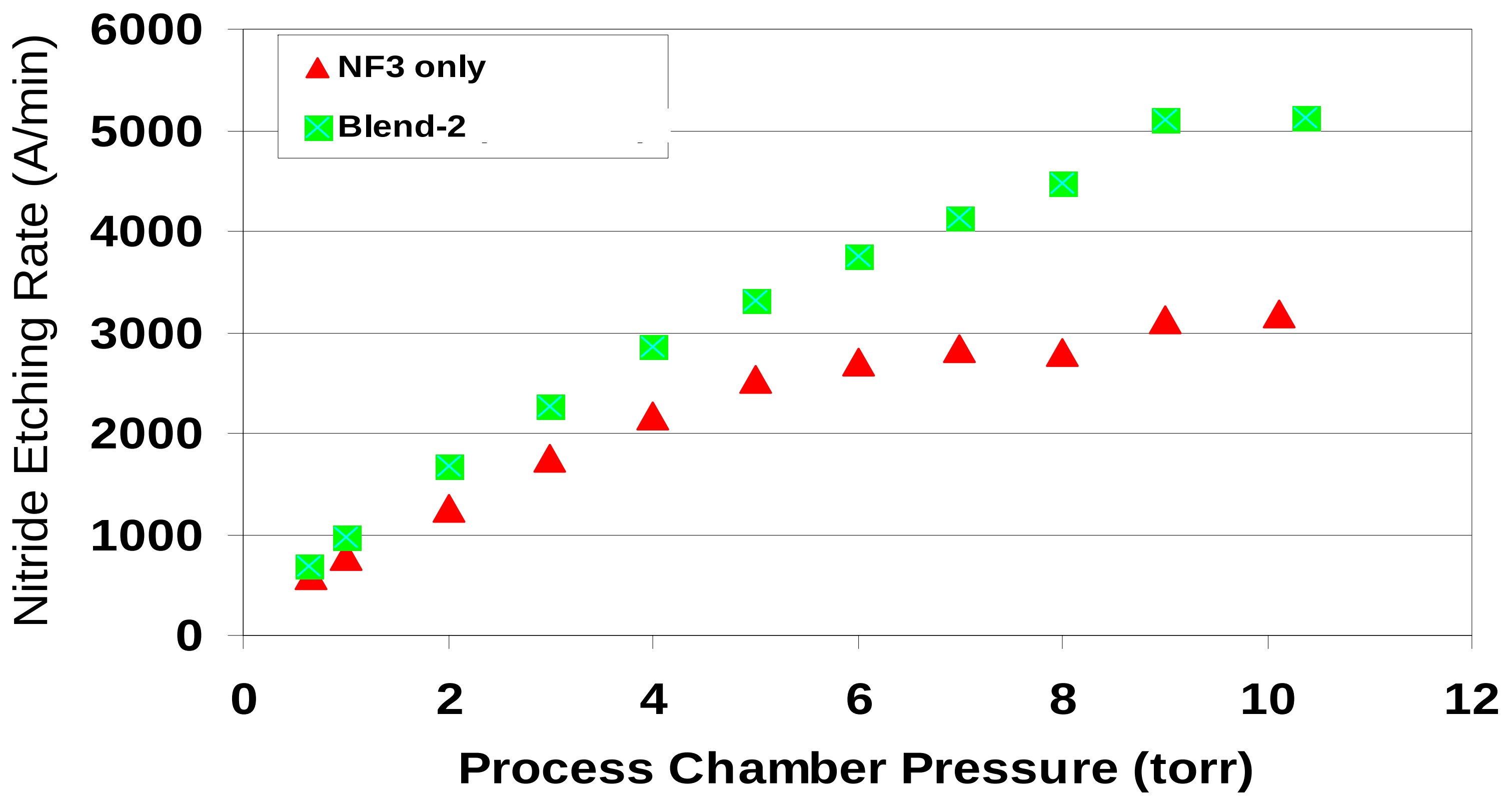
- **Blend-2 does not have advantage in etching rate on Oxide Film**

Process Chamber Pressure



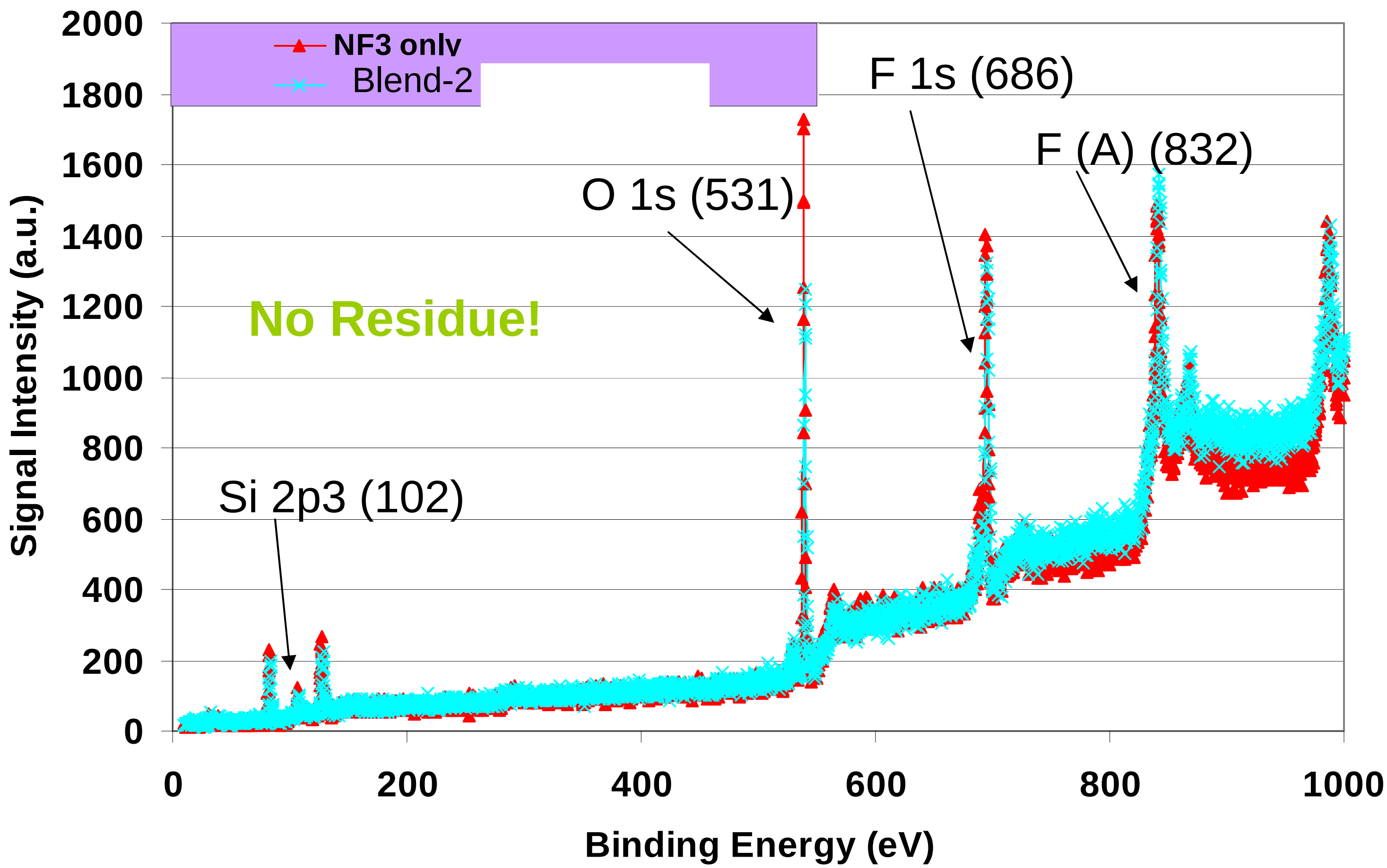
- **Blend is dominant over straight NF3**
- **$P_{plasma\ source}$=15 torr (almost constant, choked flow)**
- **$T_{electrode}$=100˚C, Q_{flow} =4800 sccm**

Process Chamber Pressure



- **Blend is dominant over straight NF_3**
- **$P_{plasma\ source}$=15 torr (almost constant, choked flow)**
- **$T_{electrode}$=200°C, Q_{flow} =4800 sccm**

XPS Surface Analysis



- **After running for 30 min, no significant residue on sapphire surface**

Acknowledgement

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