Process Models for the Reduction of High GWP Gases

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Contents

Global warming potential of selected gases

- Global warming potential (GWP) values for 100-year time horizon from IPCC Fifth Assessment Report, 2014 (AR5) .

Gas	GWP
CO_2	1
CH_4	28
CHF_3	12 400
CF_4	6 640
C_4F_8	9 540
NF_3	16 100
N_2O	265
SF_6	23 500

EU regulation No 2024/573 (2024-11-03)
Article 16 Reduction of the quantity of hydrofluorocarbons placed on the market
1. The placing on the market of hydrofluorocarbons shall be allowed only to the extent that producers and importers
have been allocated quota by the Commission as set out in Article 17.
Producers and importers placing hydrofluorocarbons on the market shall not exceed the quota available to them at the moment of placing on the market.
2. Paragraph 1 shall not apply to hydrofluorocarbons that are:
...
(e) supplied directly by a producer or an importer to an undertaking using it for the etching of semiconductor material or the cleaning of chemicals vapour deposition chambers within the semiconductor manufacturing sector.

And comprehensive reporting !

Outlook

- Current law:
  REGULATION (EU) 2024/573 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 7 February 2024 on fluorinated greenhouse gases, amending Directive (EU) 2019/1937 and repealing Regulation (EU) No 517/2014.

- Greenhouse gases (GHG) as SF_6, C_4F_8, NF_3 are expected to be charged (at least partially) proportionally to their Global Warming Potential (GWP).

- Biggest impact by:
  - Deep Silicon Etching (MEMS, Bosch,..)
  - Chamber Cleaning (PECVD, NF_3,...)

- The semiconductor industry is still excepted.

- The current EU regulation does not include the announced fee of 5 later 3 € / t CO_2 equivalent. For a typical MEMS fab with 3 t / a SF_6 → 211 500 € / a. This would increase the gas cost from below 1 € per process for a typical Bosch process up to 2...3 €.

- This is only a break !
  There will be no SF_6 producer any longer in Europe → Costs will rise.

→ Process and cost analysis incl. risk estimation

Chemical Process Models solve Process and Environment issues ...

Decreasing etch rate within Wet Clean cycles

Issues with large open area

Chemical process model

Increase of gas utilization, reduction of exhaust for environmental protection

Large gas consumption as for PECVD cleans & cost reduction

… and leads to the right questions

- Is the process transport or surface reaction controlled ?
- The etch rate (ER) of a transport controlled process depends mainly on gas flow and slightly on source power.
  Chamber wall condition controls depletion of reactants at the wafer.
- How much of the process gas is really used for the etching or deposition at the surface ?
- In particular important for high ER processing as DRIE or plasma clean after dielectric deposition.
  → Cost saving potential, often recipes are created by copy and paste.
- What is the expected flow of byproducts at the exhaust ?
- Improvement of exhaust handling and reduction of global warming potential

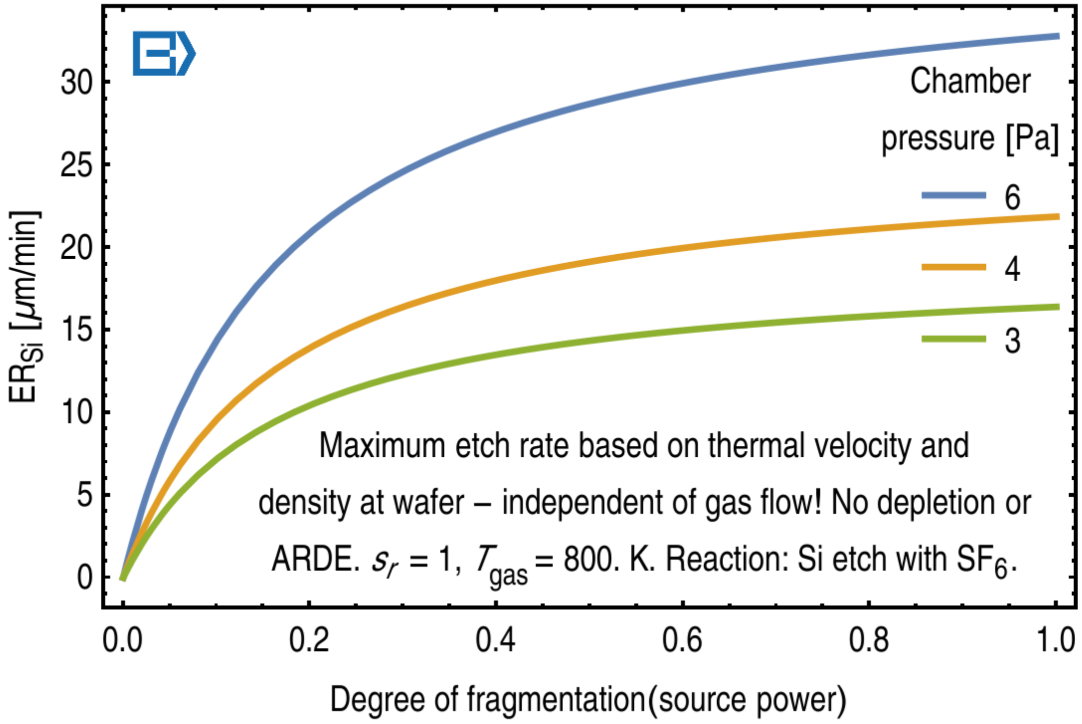
Approaching the process reality – basic analysis

- Pressure and stoichiometry are needed to calculate the gas flow ratios.

- Example: Si etch in Bosch process
  - Gas phase reaction: **$SF_6 \rightarrow 6\ F + S$**
  - Surface reaction: **$4\ F + Si \rightarrow SiF_4$**

- Basic analysis delivers the Maximum Etch Rate (ER), depending on pressure only.

- A comparison with the measured etch rate gives a first idea of the:
  - fragmentation of process gas
  - loading (depletion of etchants) at wafer, and
  - ARDE.



Simple Process Model

- Gas flow and gas phase reaction
  → Amount of reactants

- Information needed:
  - etch rate
  - open area

- Surface reaction model provides, assuming full fragmentation:
  - Balance of process gas flow and reactants lost at wafer surface leading to byproduct flow and flow of unused and fragmented process gas.

→ Gas utilization factor

Recipe A6 with Puls and Ramps – Cost Analysis

- Duration: 10.94 min.
- Trench depth: 30 µm
- Trench width: 2.6 µm
- Open area: 0,3%
  - **AR_{max} = 11.5 µm/min**

- Measured Cumulative
  - **ER = 2.8 µm/min**

- Mean step length, Si etching assumed in last step only:
  $ER_{Si} \approx$
  $(1.5 + 1.0 + 3.7) / 3.7 \cdot 30$ µm /10.94 min
  = 4.6 µm/min

- Pure gas costs per process without clean and disposal, appr. 350 sccm SF_6, 240 sccm C_4F_8
  - C_4F_8 0,32 €
  - SF_6 0,49 €

- The charge of 3 €/t CO_2 equivalent was planned but removed in the final regulation.
  - Despite this, the price of SF_6 will rise. The last producer in Europe of SF_6 stopped already production.

Process Analysis: Recipe A6

- Mean bond energy S-F = 3.3 eV
  Minimum energy necessary for full breakdown of SF_6
  → 19.8 eV / Molecule
- Losses in coil and matchbox assumed: 30%.
  Therefore, 28 eV are needed for full dissociation.
- 50% more energy as needed for full fragmentation.
  → Power could be reduced from 2.5 kW to 2 kW.

The SF_6 flow is much too high for this tiny open area.

Chamber:	SPTS DSi 150 mm
Reaction:	Si etch with SF_6
Process:	Bosch 150, Rec. A6 :Trench:ResistMask:0.3%
	380sccm, 2.5kW, 3.7s Si etch
Substrate diameter [mm] =	150.
ER / Depo rate [nm/min], Open area =	{4595.09, 0.003}
$p_{Chamber}$ [Pa], P_{source} [W] =	{5.32, 2500}
Inward flux of process gas SF6 [sccm] =	380
Process gas flux directly used SF6 [sccm] =	0.304
Utilization factor process gas SF6 [%] =	0.08
Energy per molecule P_{source} / $I_{gas,total}$ [eV] =	91.8
Exhaust unused, main process gas F [sccm] =	2280.
Exhaust fragmentation byproduct S [sccm] =	380
Exhaust surface react. byproduct SiF4 [sccm] =	0.456

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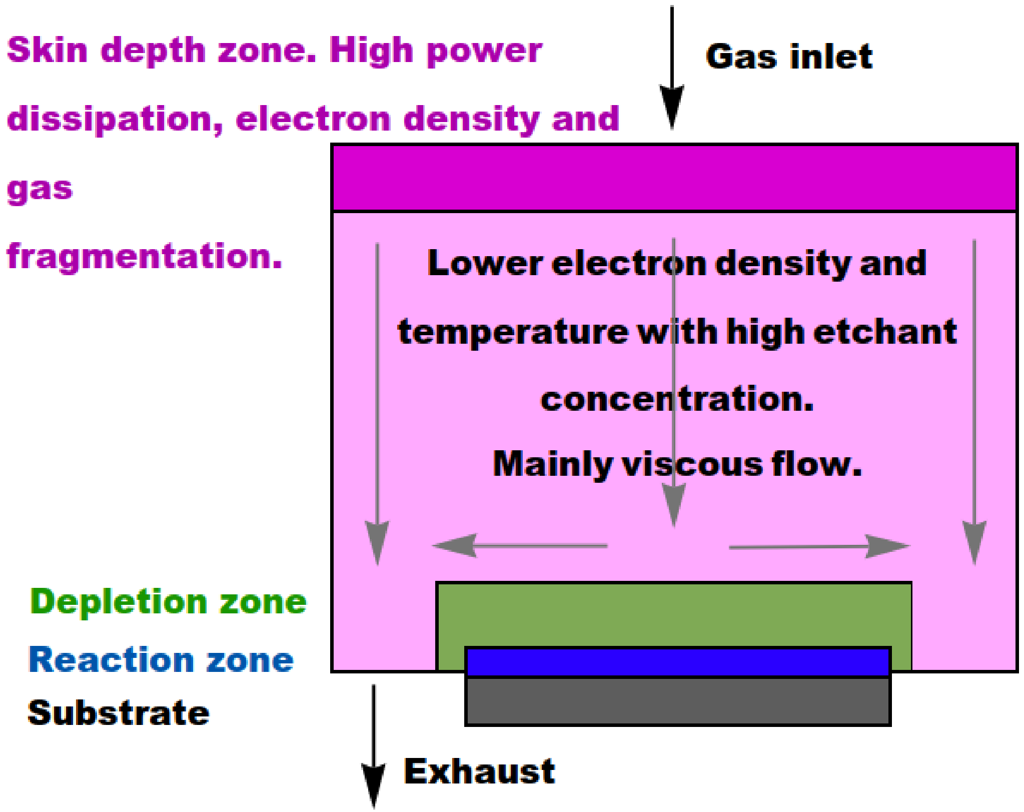
Extended Process Model

- Saving of process gas and reducing costs and emission of climate-relevant gases.

- Process stability
  - Higher Uptime
  - Minimizing of side effects when saving process gas
    - Fitting the transport from source to wafer
    - Sufficiently fast gas exchange (residence time) also with reduced gas flow → sidewall roughness
    - Sufficient exchange of reactants and byproducts at wafer



Process Analysis: Recipe A6 – Fragmentation

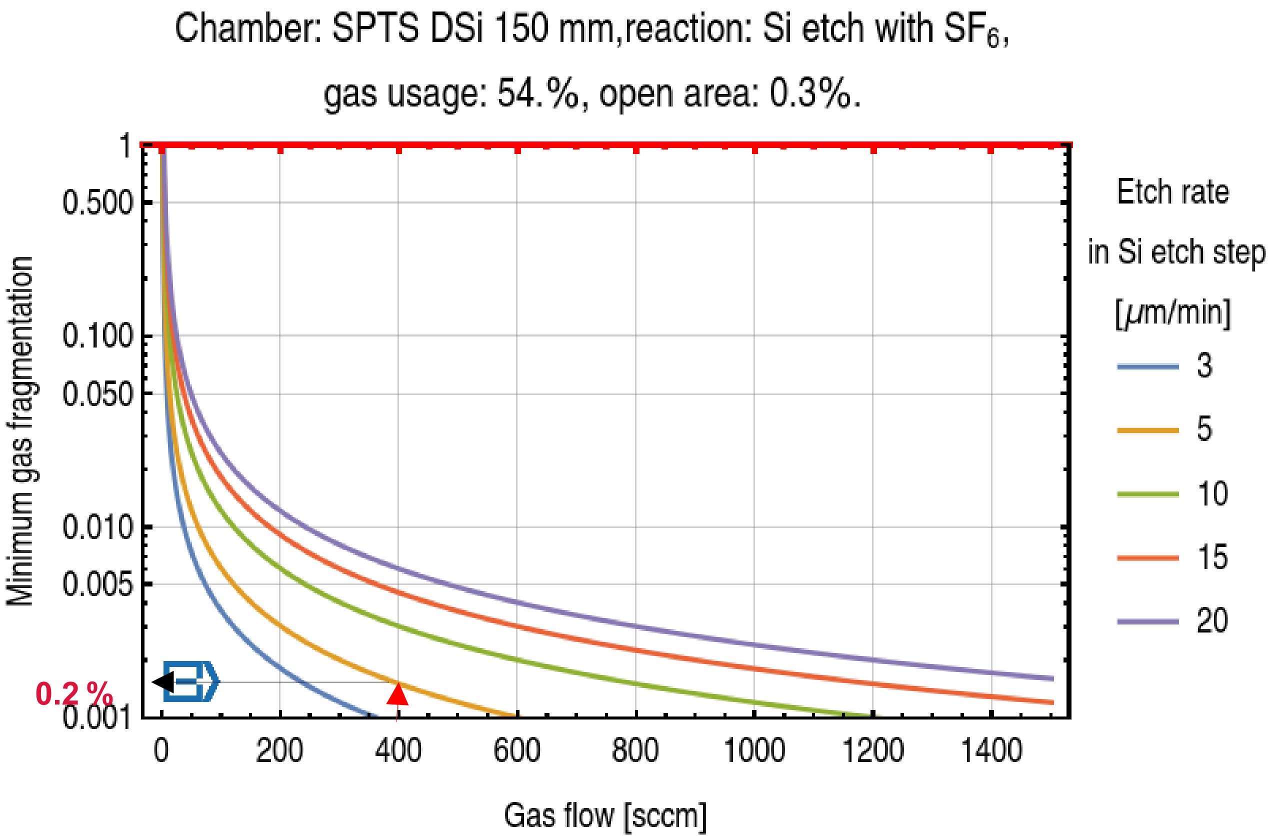
- The etch rate of the Si Etch step is 4.6 µm/min (see last page), orange curve. The process is using 380 sccm of SF_6 .

- To reach the measured ER with the gas flow set point of 380 sccm, only 0.2 % fragmentation is required.

- This means that large amounts of reactive species flow in the the vacuum system without reacting with the wafer!!!

- A huge cost saving potential of SF_6 Is found

  Loss of process gas passing the wafer is estimated. The higher the etch rate or the smaller the flow, the higher the fragmentation (source power) required.



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Recipe A6 with Reduced SF_6 Flow – Process Results

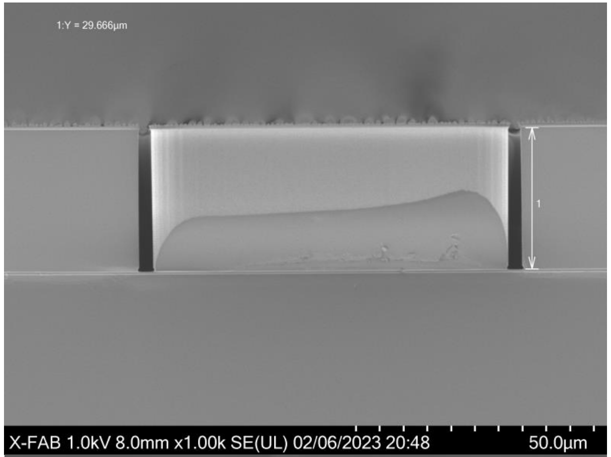
- Ansatz: Keep total gas flow constant.
  → Gas temperature

- E11:
  Ramp 330 sccm SF_6 → 230 sccm SF_6 + 100 sccm Ar

- E12:
  Ramp 430 sccm SF_6 → 330 sccm + 100 sccm Ar

- ER – no significant difference in etch depth:

Original Process:	29.7 µm
Optimized Process:	29.3 µm



Minimize Throttle Valve Movement – longer use of non consumable Parts

- One target of the recipe assessment: The ratio of pressure and gas flow should be similar – in order to reduce the control response for the throttle valve over all process steps in the loop (polymer deposition, polymer etch, Si etch.
- Targets:
  - Process stability
  - Reduced wear of hardware

Ref: Plasmetrex Plasma School, M2 Process Fundamentals, ©Plasmetrex 2024

Throttle valve position as indicator

- If the gas is heated by fast ions in the sheath also the chamber wall (liner) gets hot. Then the sticking probability of the gas is reduces, the gas looses less heat at the chamber wall, the gas temperature increases again.
- In order to keep the pressure constant, the gas flow conductance L must be increased

$$p_{gas} = \frac{q_{pV}(T_{gas})}{S_{eff}} = q_{pV}(T_0)\,\frac{T_{gas}}{T_0}\left(\frac{1}{S}+\frac{1}{L}\right)$$

→

If the throttle valve opens, gas temperature increase is one of the possible root causes.

- Other root causes:
  - Higher process gas flow (recipe)
  - More byproducts due to higher etch rate or changed deposition rate.

From Plasmetrex' Advanced Vacuum Course, © 2018

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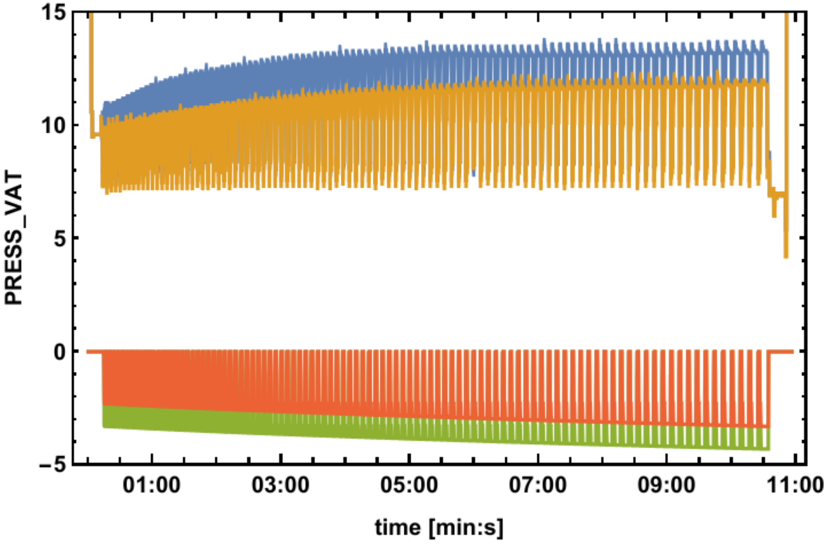
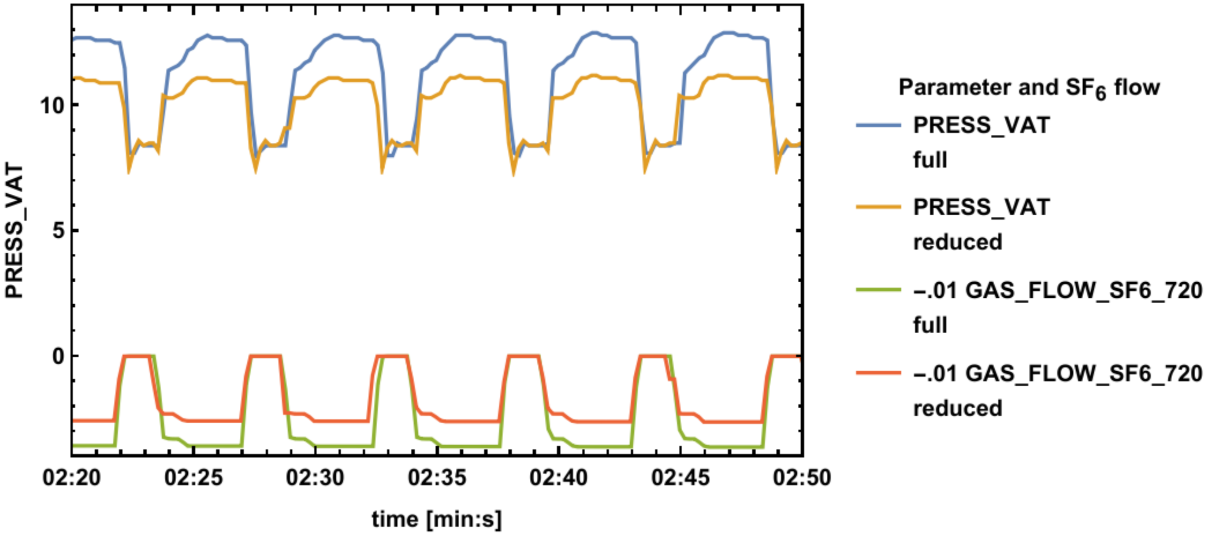
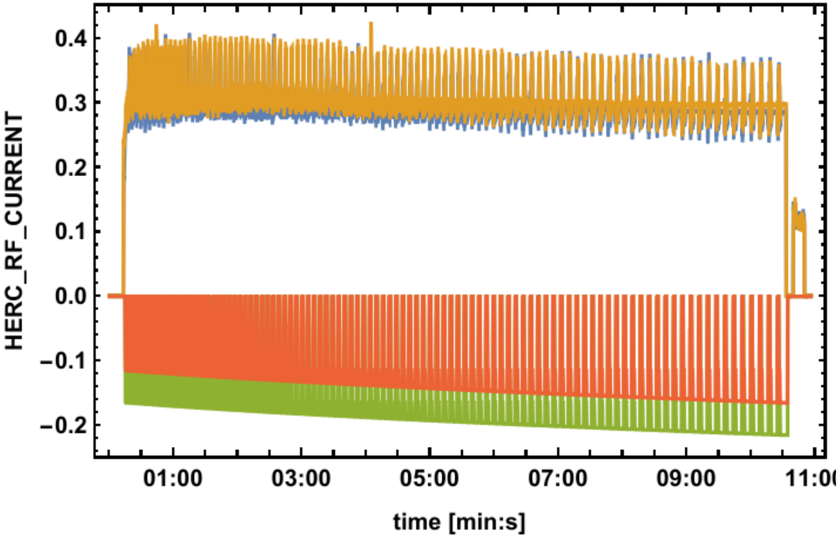
Process Comparison A6 with & w/o Reduced SF_6 Flow – Throttle Valve

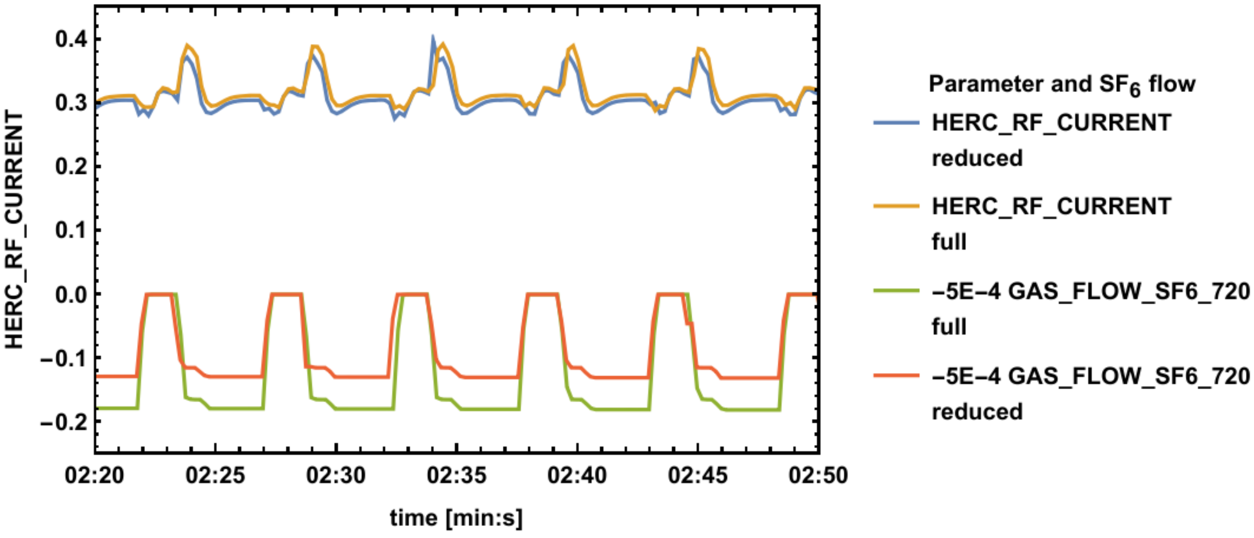




- E11: 330 sccm SF_6 replaced by 230 sccm SF_6 + 100 sccm Ar
  E12 ramp 330 → 430 sccm replaced by ramp 230 → 330 sccm + 100 sccm Ar.
- **Pumping speed for Ar obviously higher as for F and S.**
- Pressure control stable, no change in D1, reduced load of throttle valve
- Other tool parameters as V_{pp} source do no respond.
- Pressure in deposition should be slightly reduced down to 30 mTorr.

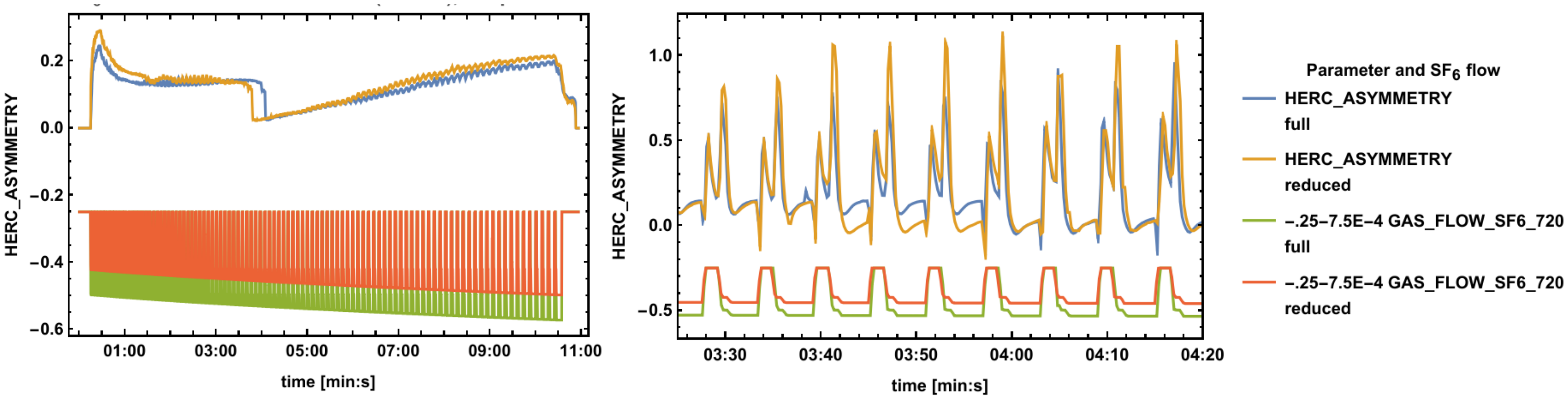
Process Comparison A6 with & w/o Reduced SF_6 Flow – Wall Current





- No difference in RF wall current flow.
- RF_PLATEN_LOADCAP → only a small response.

How much Saving Potential without Process Risk ?



- Process Comparison A6 with & w/o Reduced SF6 Flow – Asymmetry
- Mean plasma Asymmetry changes after 4 min, with full gas flow a bit later. Also slightly visible in RF_PLATEN_LOADCAP.
- Zooming in shows the change occurs only in the Si etch step. Reason not known.
- Conclusion: Reduction of SF_6 flow does not influence plasma parameters nor the ER, very stable process.
- Proposal: No ramp, further SF_6 reduction down to const. 250 sccm.

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Summary: Gas Flow Reduction and Process Stability

- There are always three main questions
  - Is the process transport-controlled? — In DRIE usually yes.
  - Is the gas flow appropriate? — → Gas usage
  - Is the source power high enough? — → Energy per molecule

- The chemical process analysis shows for almost all process high gas saving potential.

- Results from the experiments:

  - The control response of the throttle valve can be reduced → higher live time.

  - Plasma parameters are an early indicator for significant process changes
    No change of wall current → same ion energy
    Other parameters are more sensitive to changes, when the gas usage is higher.

  - Despite slight change in plasma parameters → ER and CD are still fine.