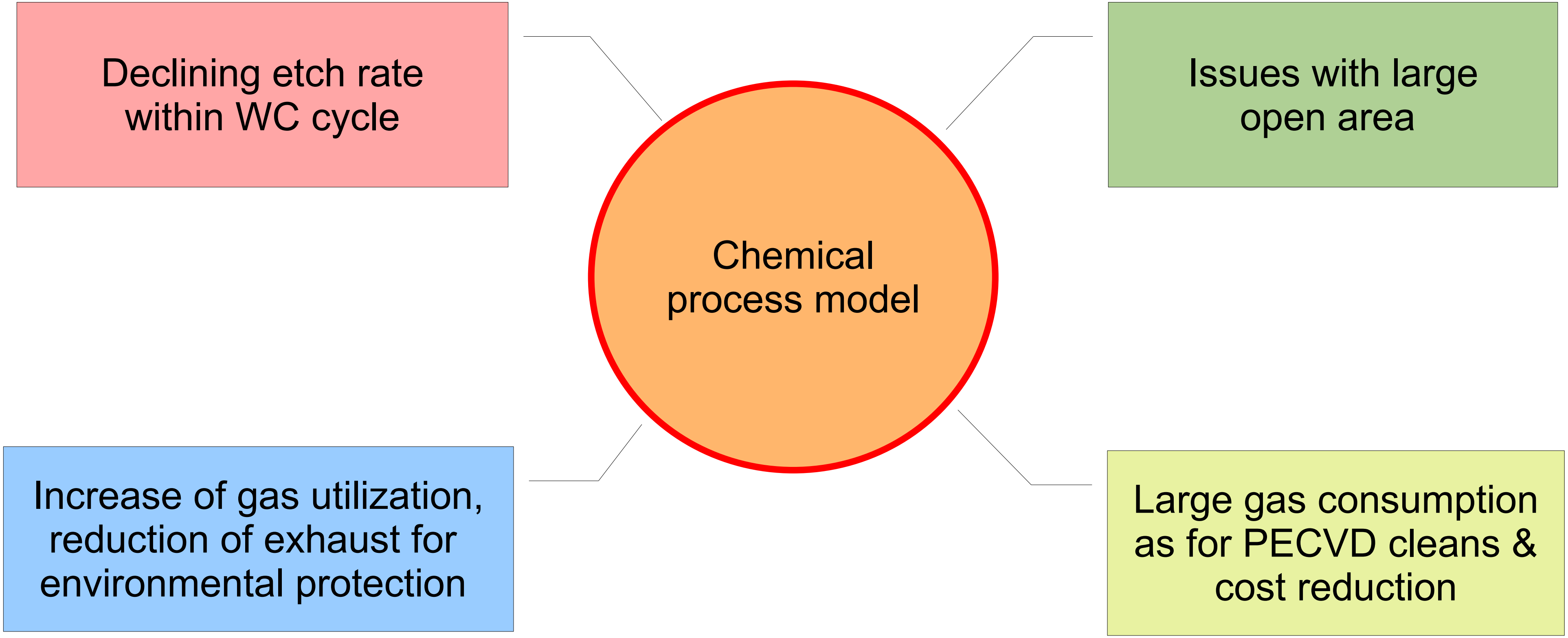
Chemical Process Models

Michael Klick, Dirk Suchland, Lutz Eichhorn
Plasmetrex GmbH

Process and environment issues solved by chemical process model



Declining etch rate within WC cycle

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 ?
- How much of the process gas is really used for the etching or deposition at the surface ?
- What is the expected flow of byproducts at the exhaust ?

- 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.
- In particular important for high ER processing as DRIE or plasma clean after dielectric deposition.
  → Cost saving potential
- Improvement of exhaust handling and reduction of global warming potential

Global warming potential of selected gases

EU regulation No 517/2014: By 2030 the EU will cut the F-gas emissions by two-thirds compared with 2014 levels (https://ec.europa.eu/clima/policies/f-gas_en).

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

In article 15, there is currently an exception for etching and dry cleans in the semiconductor industry. But one can expect this to be changed after 2030 latest.

Global warming potential (GWP) values for 100-year time horizon from IPCC Fifth Assessment Report, 2014 (AR5), https://www.ipcc.ch/pdf/assessment-report/ar5/wg1/WG1AR5_Chapter08_FINAL.pdf (p. 73-79).

Approaching the process reality in two levels

- Simple model including
  - Process gas fragmentation in source assuming full fragmentation
  - Surface reaction
  - Balance of process gas flow and reactants lost at wafer surface, based on etch rate and open area, leading to byproduct flow and flow of unused and fragmented process gas
  - All flows in sccm.

- More sophisticated model does not assume full fragmentation and comprises additionally:
  - Loss of reactant through real chamber geometry
  - Dependence of minimum gas fragmentation (depending of source power), gas flow, and etch rate.
  - Is needed to answer the question ”Is the process transport or surface reaction controlled ?”

Chemical reaction and automatic resolution of stochiometry

- Gas flow and gas phase reaction
  → Amount of reactants

- Surface reaction model provides the amount of
  - reactants needed for the given rate and open area and
  - corresponding byproducts

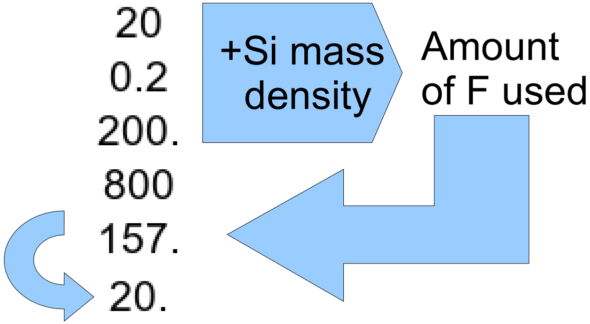
→ Gas utilization factor

- The stoichiometry is needed to calculate the gas flow ratios.

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

DRIE example: Simple process model using only available data

Chamber:	SPTS Rapier 200 mm
Reaction:	Si etch with SF_6
Process:	Bosch–Rapier, 10Pa, 800sccm, 1s, 20%
ER / Depo rate [µm/min]	20
Open area	0.2
Substrate diameter [mm]	200.
Inward flux of process gas SF6 [sccm] =	800
Process gas flux directly used SF6 [sccm] =	157.
Utilization factor of process gas SF6 [%] =	20.

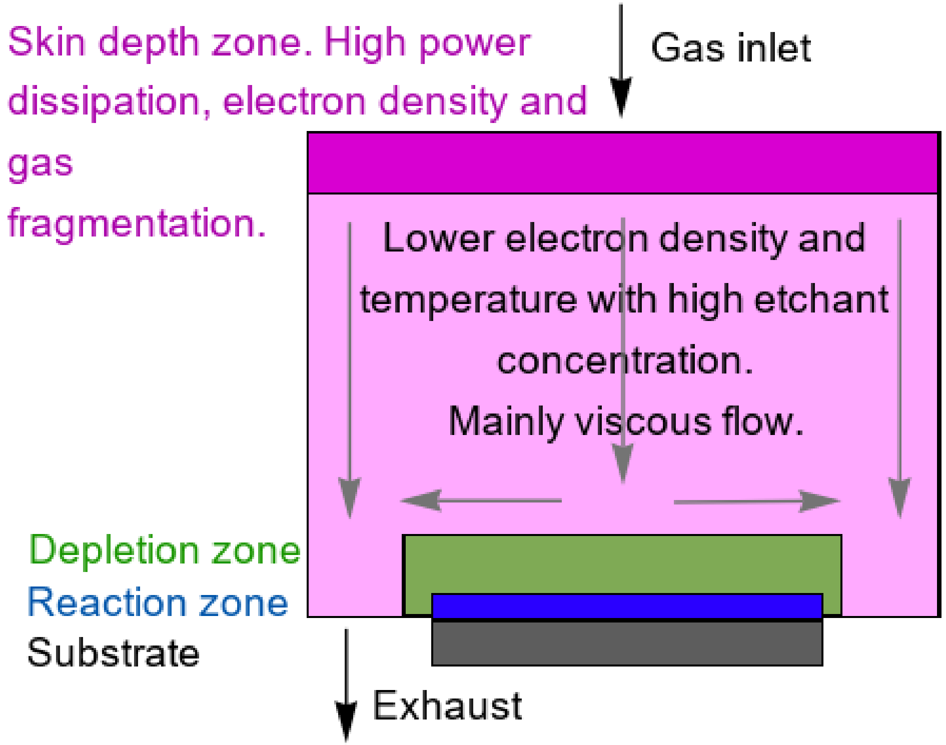


Exhaust of unused, main process gas F [sccm] =	3860.
Exhaust of gas fragmentation byproduct S [sccm] =	800
Exhaust of surface reaction byproduct SiF4 [sccm] =	235.

The etch rate is that of the Si etch step alone and needs to be recalculated from the total etch rate.

Sophisticated process model including chamber geometry

- Global model with 4 zones
- Chamber data base
- Chemical reaction data base for all usual reactions in semiconductor manufacturing used.
- Recipe and additionally open area and etch rate (ER)



Skin depth zone. High power dissipation, electron density and gas fragmentation.

Gas inlet

Lower electron density and temperature with high etchant concentration.
Mainly viscous flow.

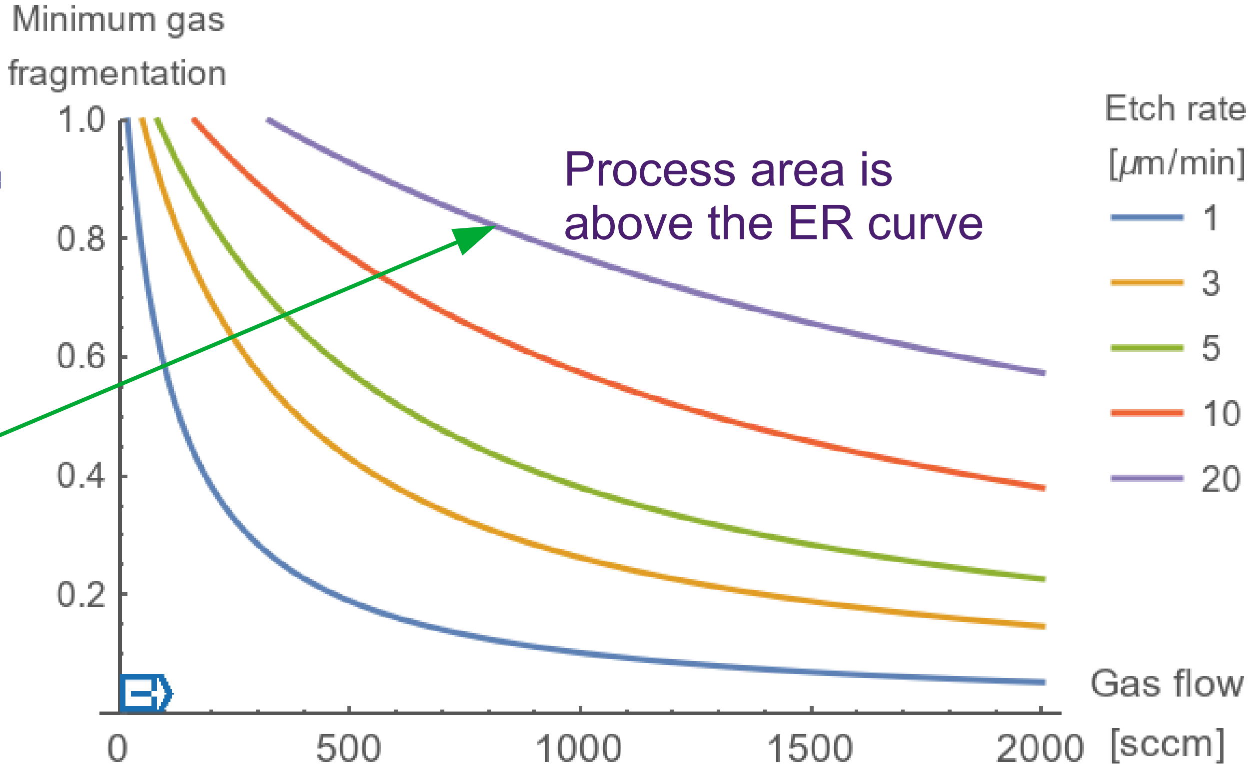
Depletion zone
Reaction zone
Substrate

Exhaust

DRIE example: Detailed analysis

- Shows basic limitation of etch rate by gas flow and gas fragmentation (source power).
- Loss of fragmented process gas by gas flow distribution – depending on ratio of wafer and chamber diameter - is here included. This loss is here about 52%.
  Not strictly transport controlled.
  No undesired influence by additional loss at chamber wall.
- Above the etch rate curve, the process is always surface reaction controlled.

Chamber: SPTS Rapier 200 mm,reaction: Si etch with SF_6, gas usage: 48.%, open area: 20.%.

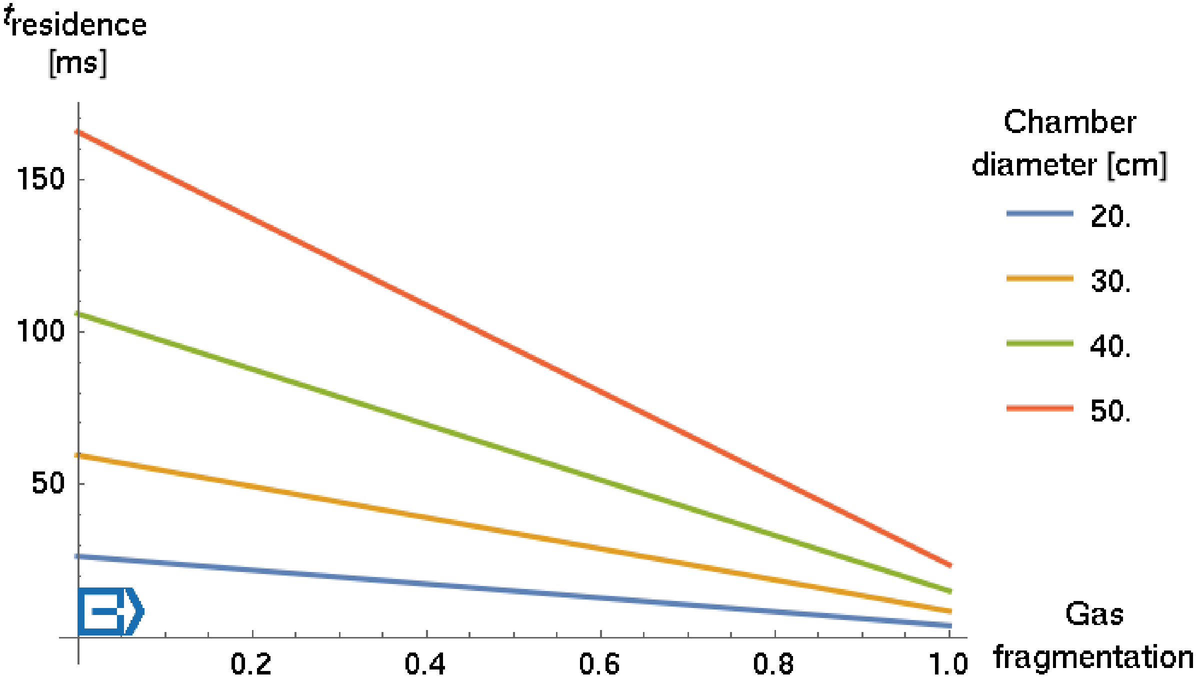


Process area is above the ER curve

Especially for Bosch Process with fast switching

- The step time must exceed the at least the double residence time in order to have well defined process conditions.
- The degree of fragmentation depends mainly on the source power.

Chamber: SPTS Rapier 200 mm
reaction: Si etch with SF_6,
total gas flow: 800 sccm.



DRIE with large open area: Process overview without chamber geometry

Chamber:	SPTS Rapier 200 mm
Reaction:	Si etch with SF_6
Process:	Bosch−Rapier, 10Pa, 800sccm, 1s, 55%
ER / Depo rate [μm/min]	13
Open area	0.55
Substrate diameter [mm]	200.
Inward flux of process gas SF6 [sccm] =	800
Process gas flux directly used SF6 [sccm] =	280.
Utilization factor of process gas SF6 [%] =	35.
Energy per molecule P_{source} / $I_{gas,total}$ [eV] =	61.1
Exhaust of unused, main process gas F [sccm] =	3120.
Exhaust of gas fragmentation byproduct S [sccm] =	800
Exhaust of surface reaction byproduct SiF4 [sccm] =	420.

Check of lack of source power

The required energy for fragmentation is approximately known.

DRIE with large open area: Transport controlled

- Due to the larger etch rate, there is always a depletion of reactants at the wafer →
  Hard transport controlled
  Decline of etch rate with higher surface roughness at chamber wall due loss of reactants.

- Here the loss of reactants by passing the wafer is included.

Chamber: SPTS Rapier 200 mm,reaction: Si etch with SF_6, gas usage: 48.%, open area: 55.%.