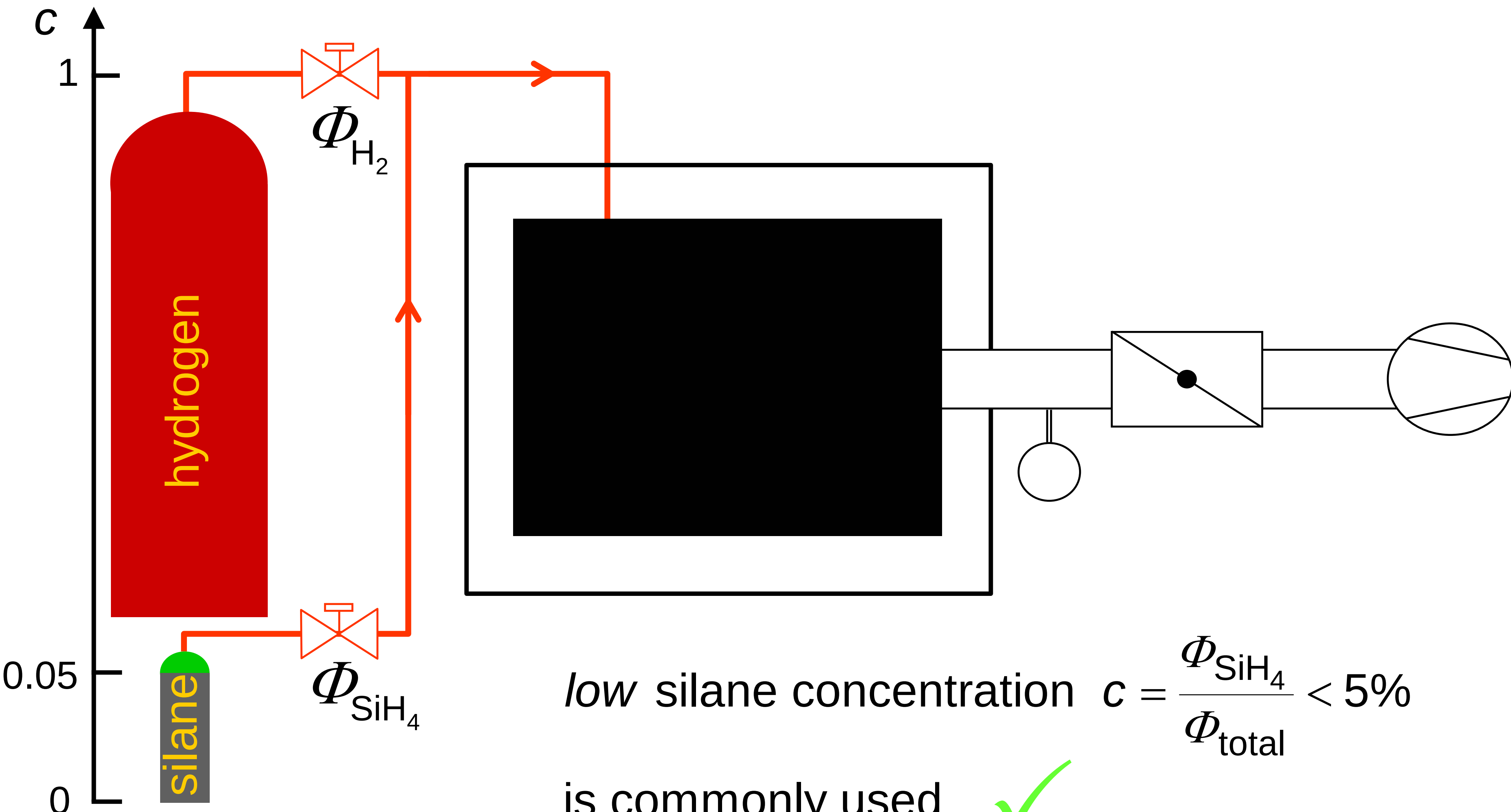
II. Zero-dimensional model. The "plasma dimension". Silane depletion. Importance of gas composition in the plasma.

III. Electromagnetic uniformity: finite RF wavelength in large area, VHF reactors.

IV. Uniformity in time: rapid equilibration to steady-state process parameters. Direct pumping of a plasma reactor.

V. So where is the problem? - Causes of non-uniformity. Some recommendations.

An example: Hydrogen dilution for plasma deposition of μc-Si:H



low silane concentration $c = \frac{\Phi_{SiH_4}}{\Phi_{total}} < 5\%$

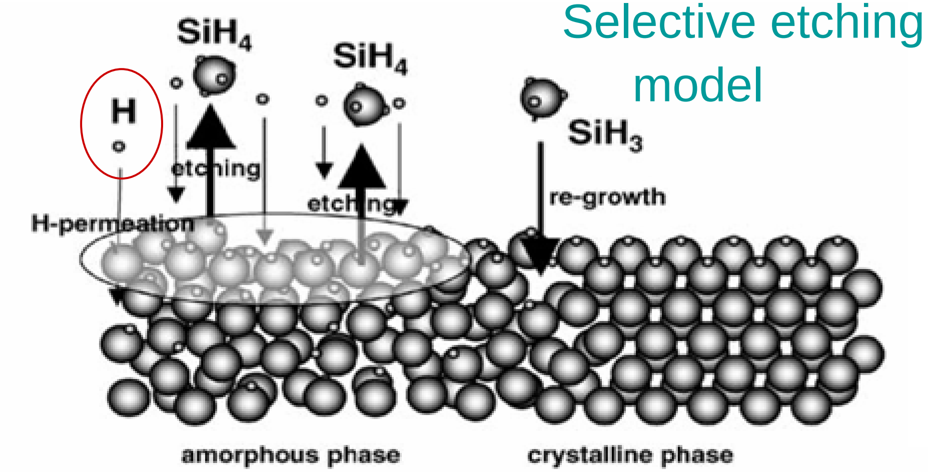
is commonly used ✓

Reason for hydrogen dilution

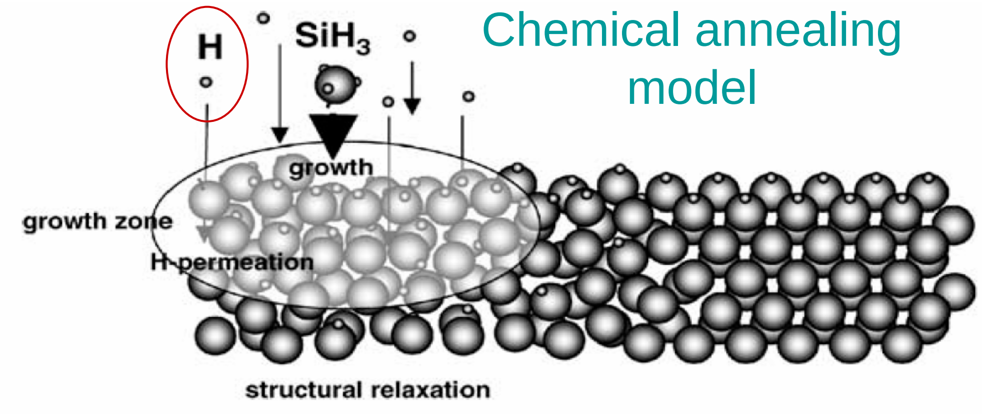
Need high ratio of H to SiH_x fluxes to deposit μc-Si:H

intuitively

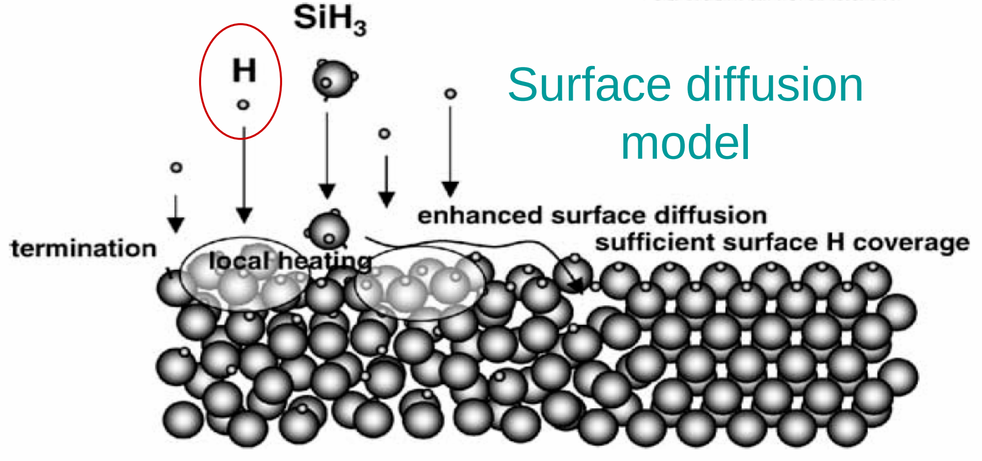
"Add more hydrogen than silane"



Selective etching model

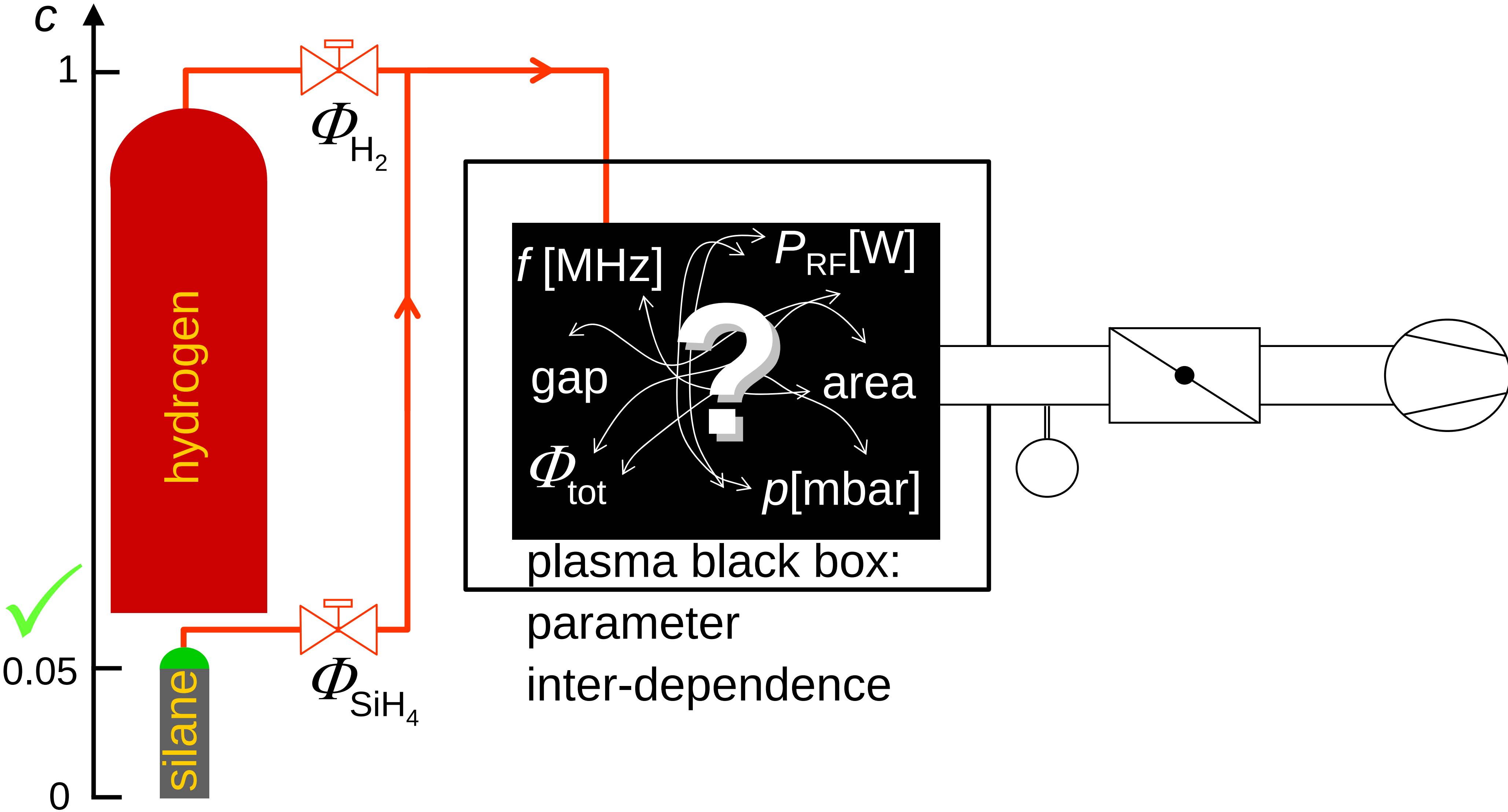


Chemical annealing model



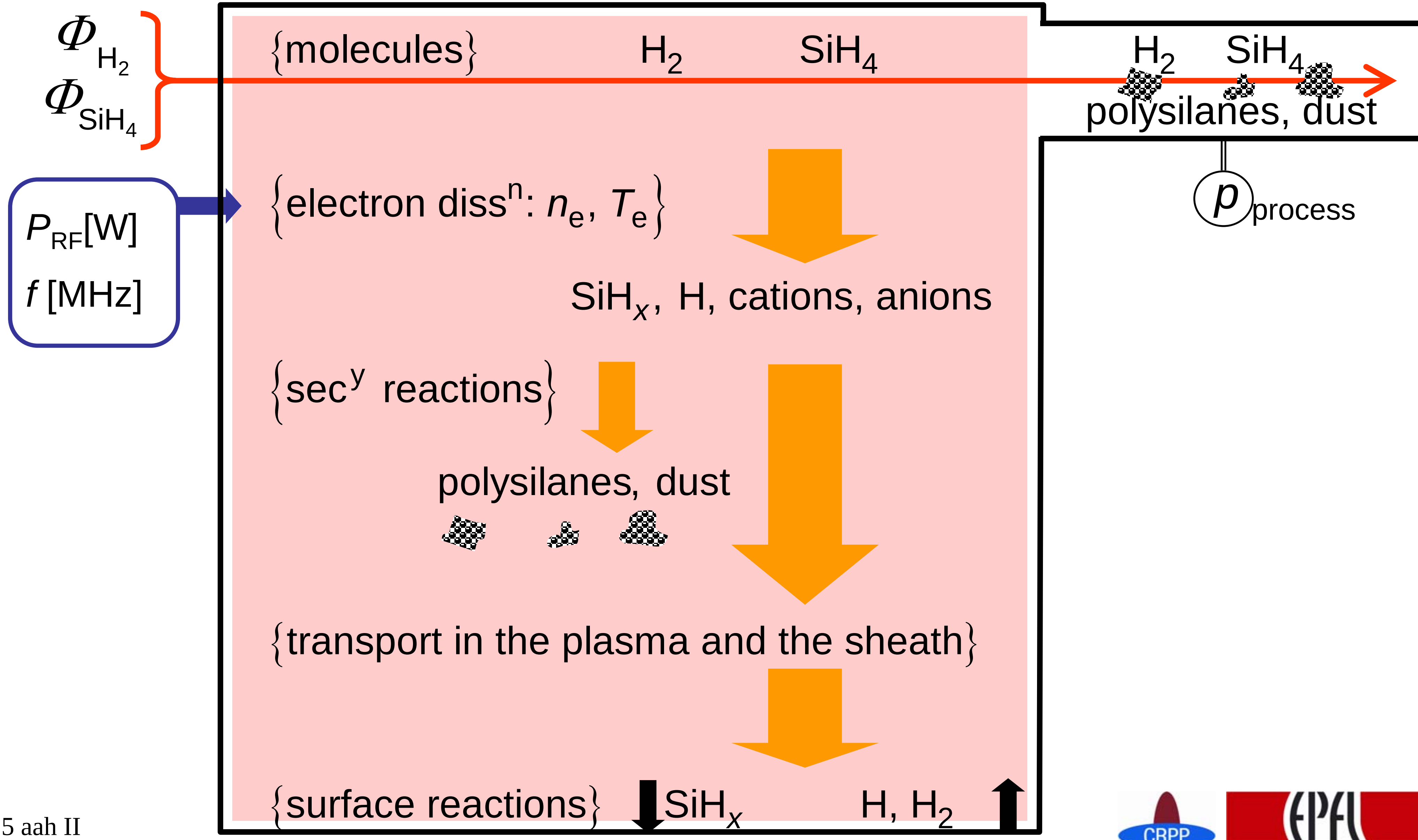
Surface diffusion model

...but the optimal *plasma* control parameters are less clear



plasma black box:
parameter
inter-dependence

...because the plasma is complex.



Φ_{H_2}

Φ_{SiH_4}

P_{RF}[W]

f [MHz]

{molecules} H_2 SiH_4

H_2 SiH_4

polysilanes, dust

$p_{process}$

{electron dissⁿ: n_e, T_e}

SiH_x, H, cations, anions

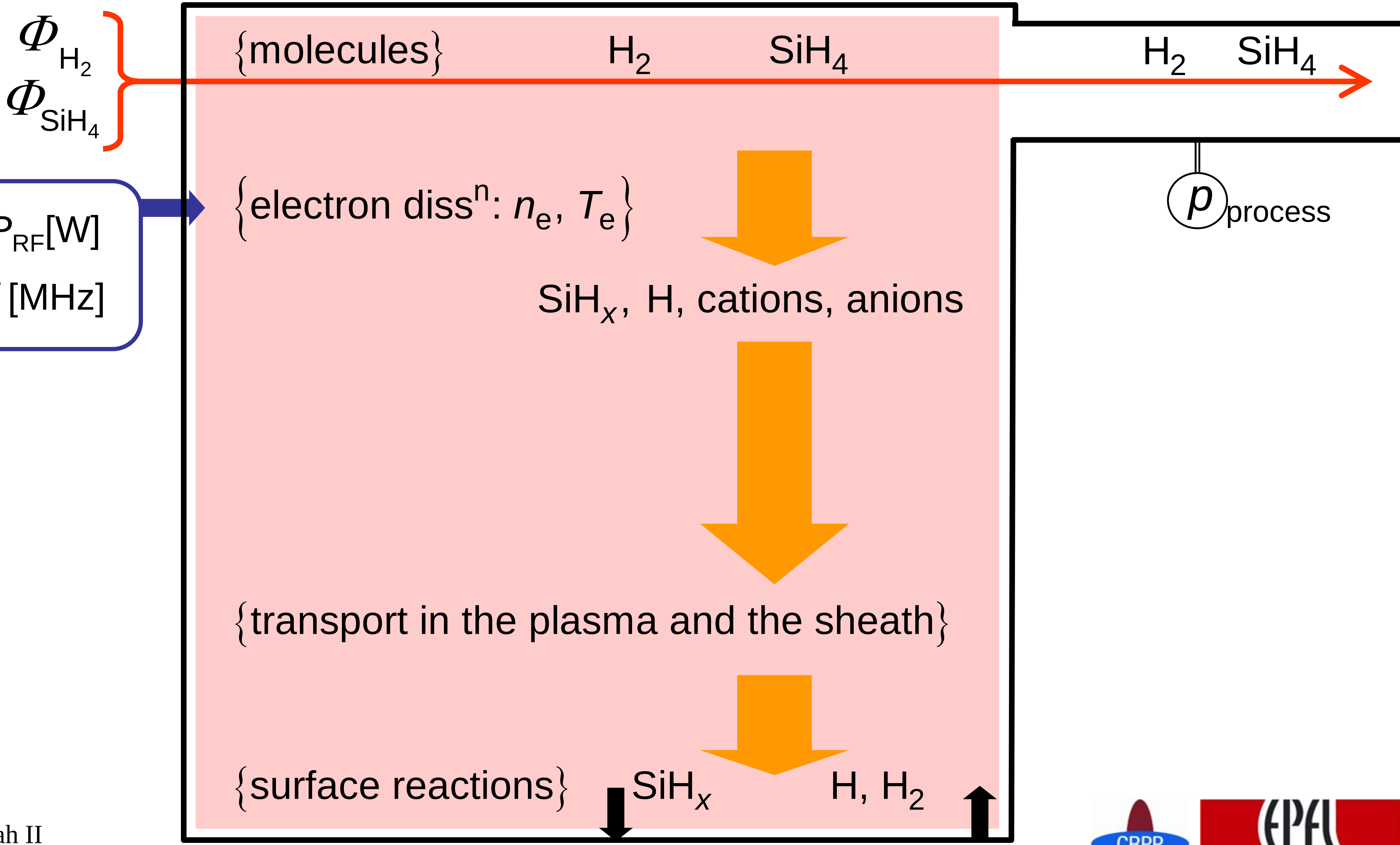
{sec^y reactions}

polysilanes, dust

{transport in the plasma and the sheath}

{surface reactions} SiH_x H, H_2

Consider low pressures (< 2 mbar)



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f [MHz]

{molecules} H_2 SiH_4

H_2 SiH_4

$p_{process}$

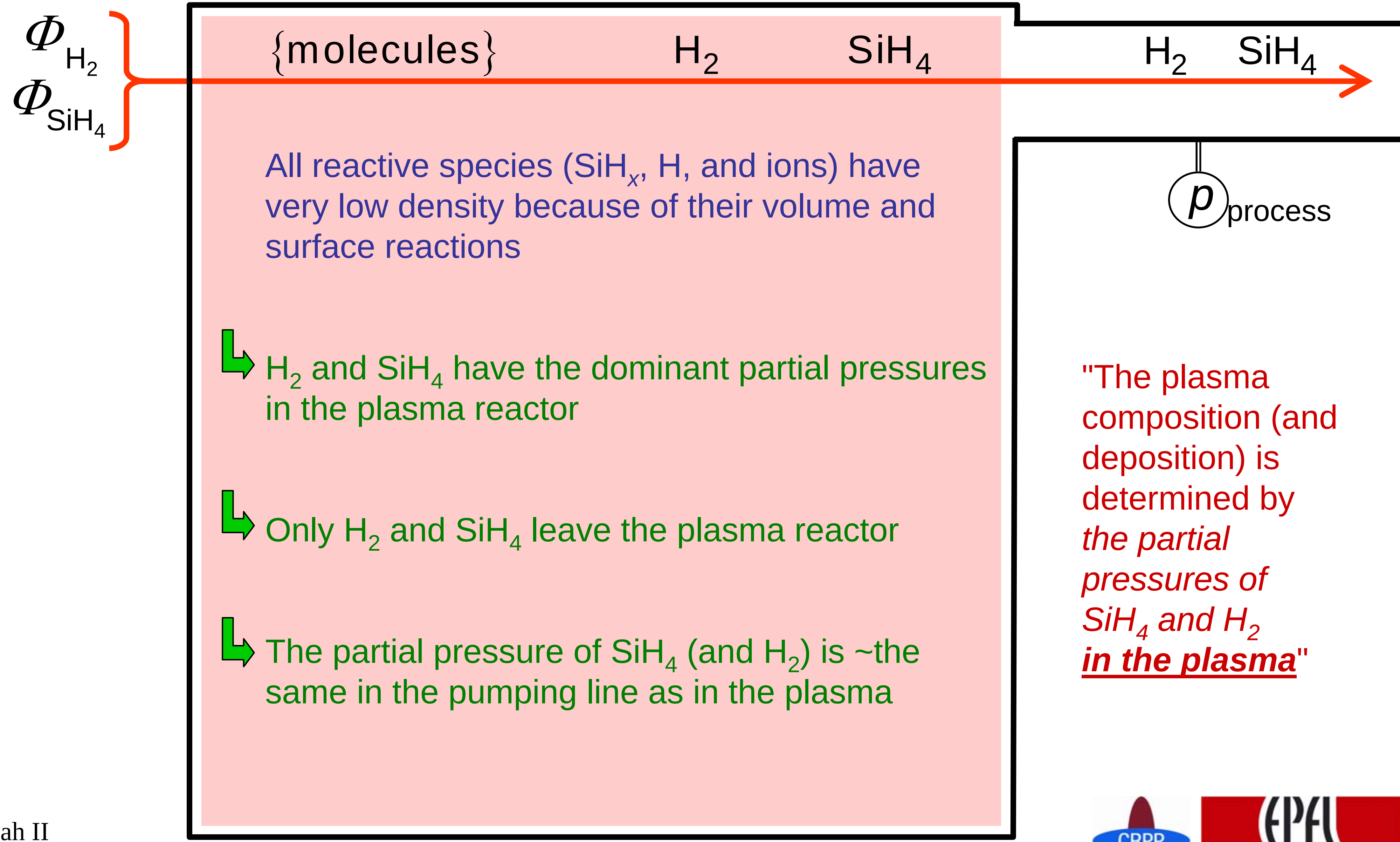
{electron diss^n: n_e, T_e}

SiH_x, H, cations, anions

{transport in the plasma and the sheath}

{surface reactions} SiH_x H, H_2

Consider only the majority species



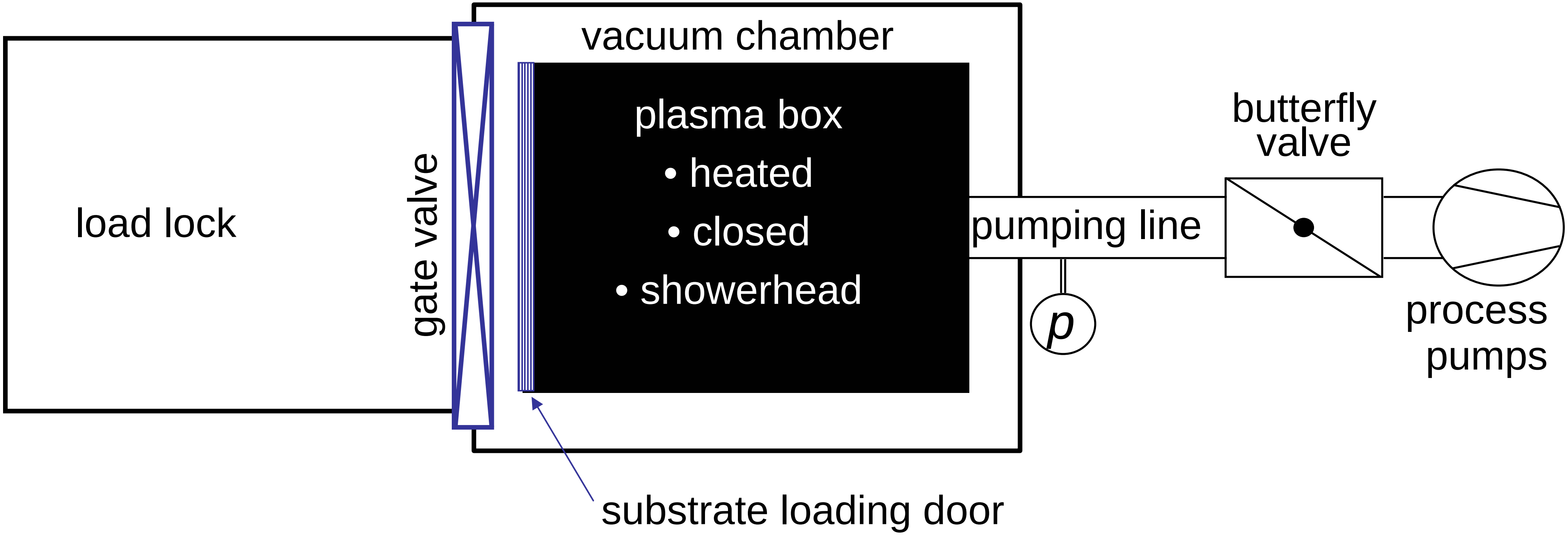
All reactive species (SiH_x, H, and ions) have very low density because of their volume and surface reactions

- H_2 and SiH_4 have the dominant partial pressures in the plasma reactor
- Only H_2 and SiH_4 leave the plasma reactor
- The partial pressure of SiH_4 (and H_2) is ~the same in the pumping line as in the plasma

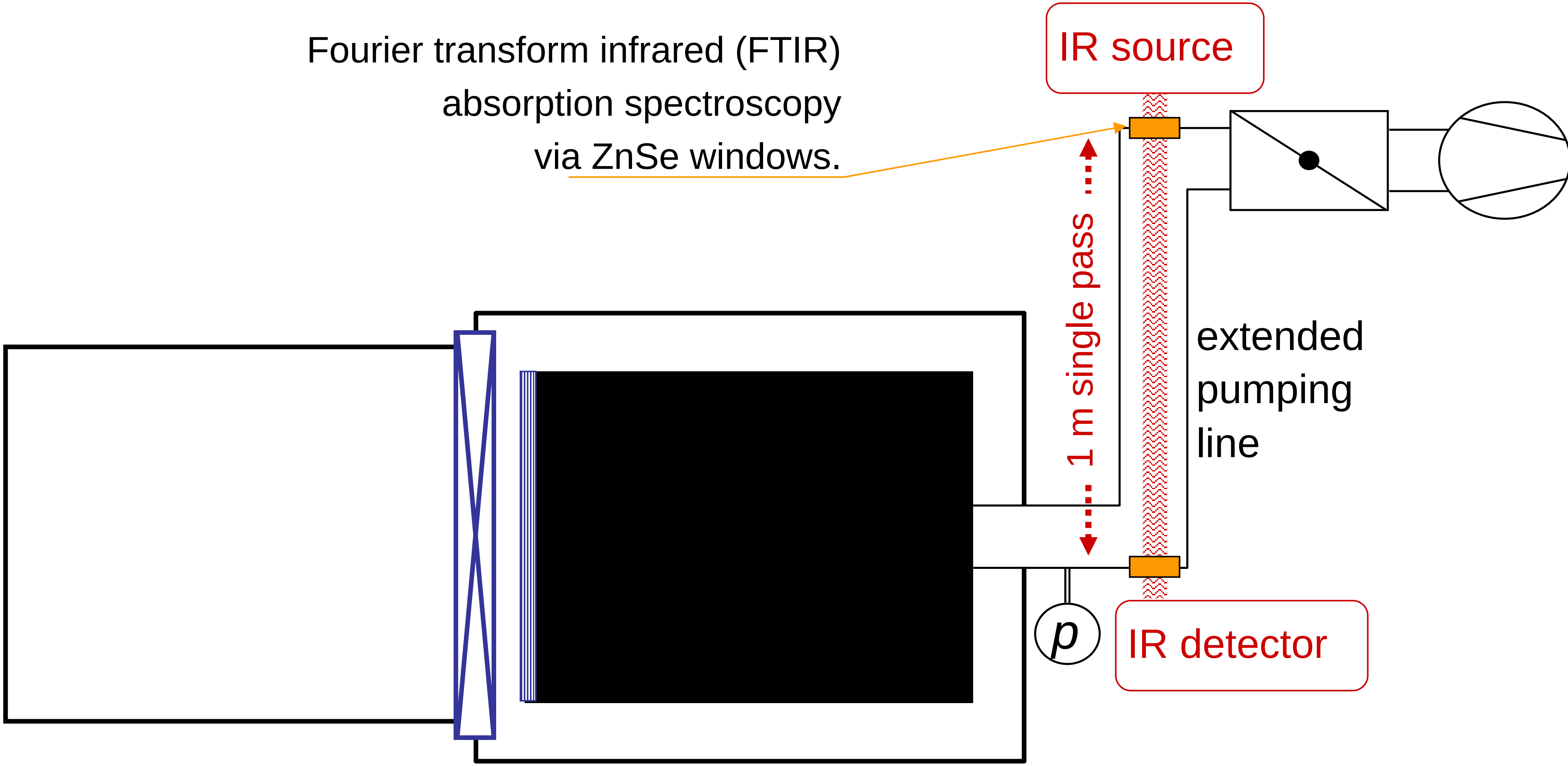
"The plasma composition (and deposition) is determined by *the partial pressures of* SiH_4 *and* H_2 ***in the plasma***"

How to measure the silane partial pressure in the plasma?

"inaccessible" plasma reactor



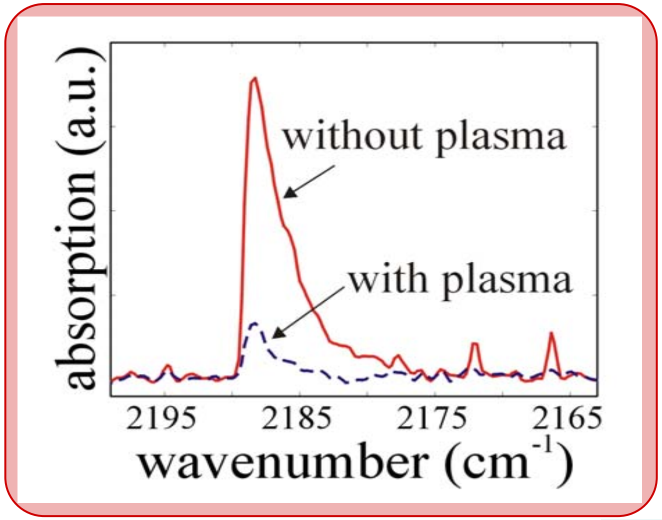
FTIR in pump line: Non-intrusive diagnostic for SiH_4 pressure

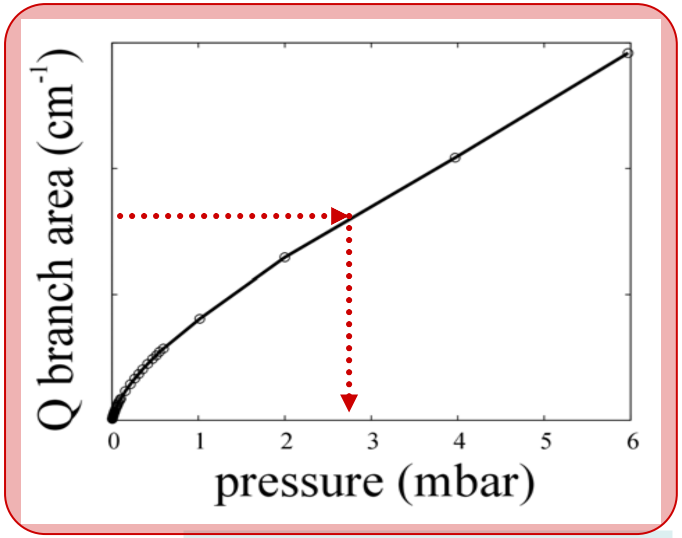


Fourier transform infrared (FTIR) absorption spectroscopy via ZnSe windows.

Silane partial pressure measurement

a) Silane infrared absorbance; *b)* Integrate spectrum; *c)* Read off a calibrated curve





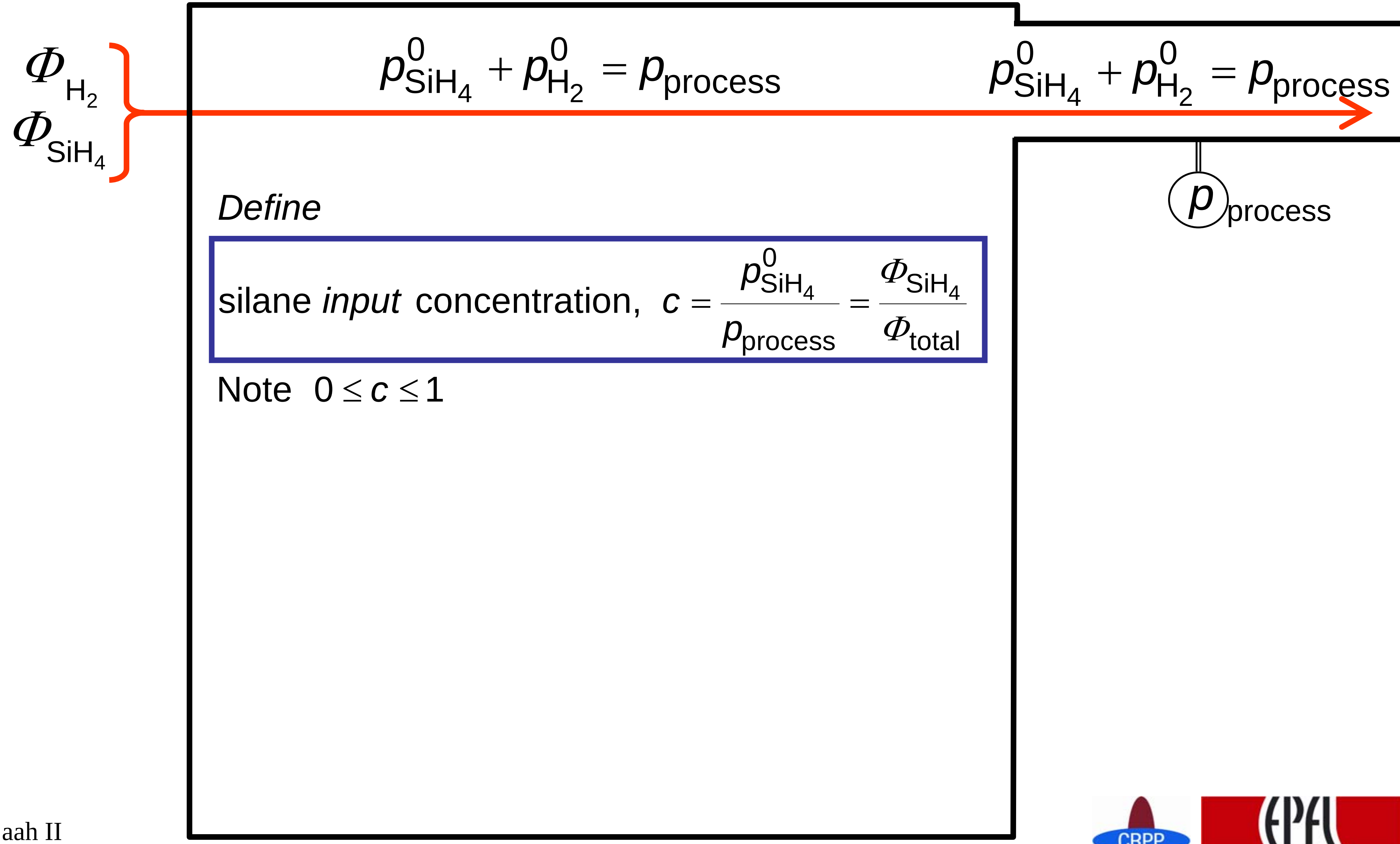
- Silane pressure with plasma < silane pressure without plasma,

$$\boxed{p_{\mathrm{SiH}_4} < p^{0}_{\mathrm{SiH}_4}} \;,$$

due to electron dissociation of silane (*irreversible loss*).

- Hydrogen partial pressure increases with plasma (silane dissociation product, surface association, & pump speed adjustment)

Silane input concentration (*without* plasma)



Φ_{H_2}

Φ_{SiH_4}

$$p^0_{SiH_4} + p^0_{H_2} = p_{\text{process}}$$

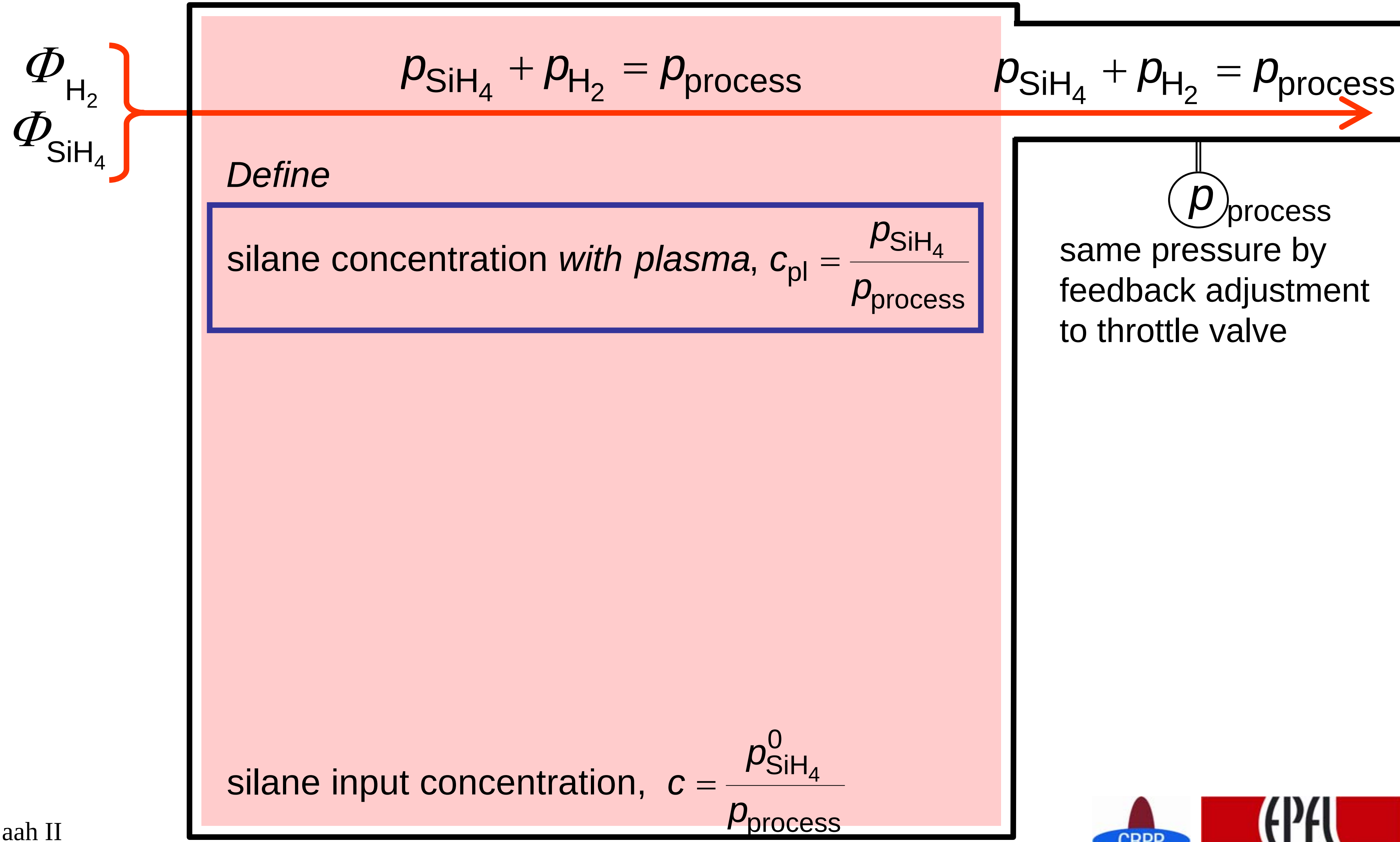
$$p^0_{SiH_4} + p^0_{H_2} = p_{\text{process}}$$

Define

$$\boxed{\text{silane } \textit{input} \text{ concentration, } c = \frac{p^0_{SiH_4}}{p_{\text{process}}} = \frac{\Phi_{SiH_4}}{\Phi_{\text{total}}}}$$

Note $0 \le c \le 1$

Silane concentration *with* plasma



Φ_{H_2}

Φ_{SiH_4}

$$p_{SiH_4} + p_{H_2} = p_{process}$$

$$p_{SiH_4} + p_{H_2} = p_{process}$$

Define

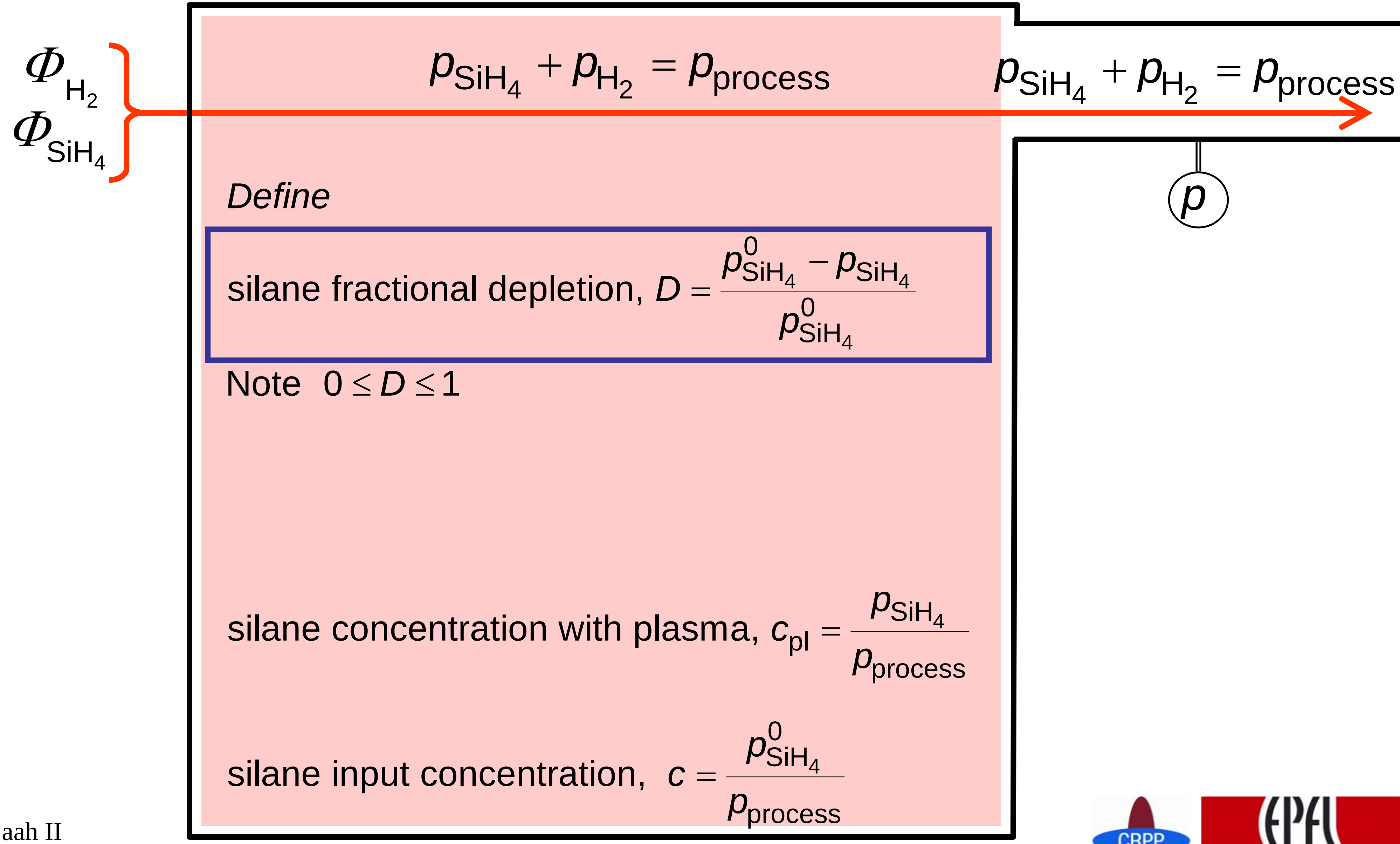
silane concentration *with plasma*, $c_{pl} = \dfrac{p_{SiH_4}}{p_{process}}$

$p_{process}$

same pressure by feedback adjustment to throttle valve

silane input concentration, $c = \dfrac{p^0_{SiH_4}}{p_{process}}$

Silane depletion due to plasma



$$p_{SiH_4} + p_{H_2} = p_{process}$$

$$p_{SiH_4} + p_{H_2} = p_{process}$$

Define

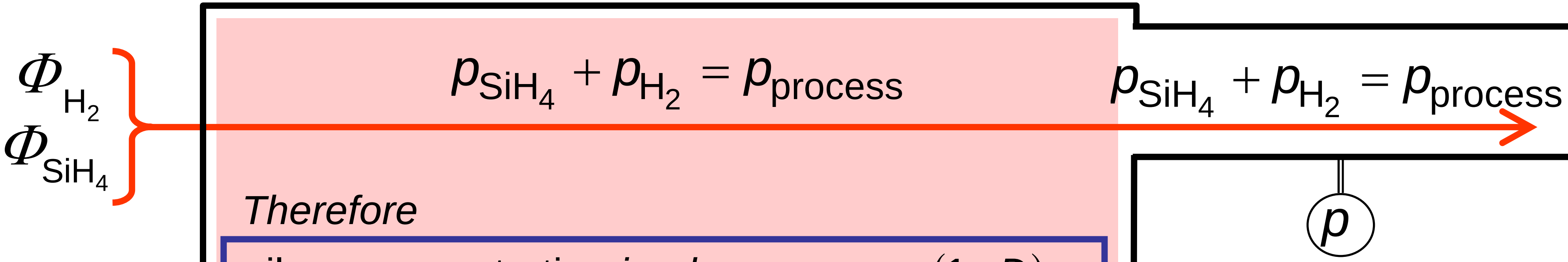
$$\boxed{\text{silane fractional depletion, } D = \frac{p^0_{SiH_4} - p_{SiH_4}}{p^0_{SiH_4}}}$$

Note $0 \le D \le 1$

silane concentration with plasma, $c_{pl} = \dfrac{p_{SiH_4}}{p_{process}}$

silane input concentration, $c = \dfrac{p^0_{SiH_4}}{p_{process}}$

Silane concentration in plasma



$$p_{SiH_4} + p_{H_2} = p_{process}$$

$$p_{SiH_4} + p_{H_2} = p_{process}$$

Therefore

silane concentration *in plasma*, $c_{pl} = c\,(1 - D)$

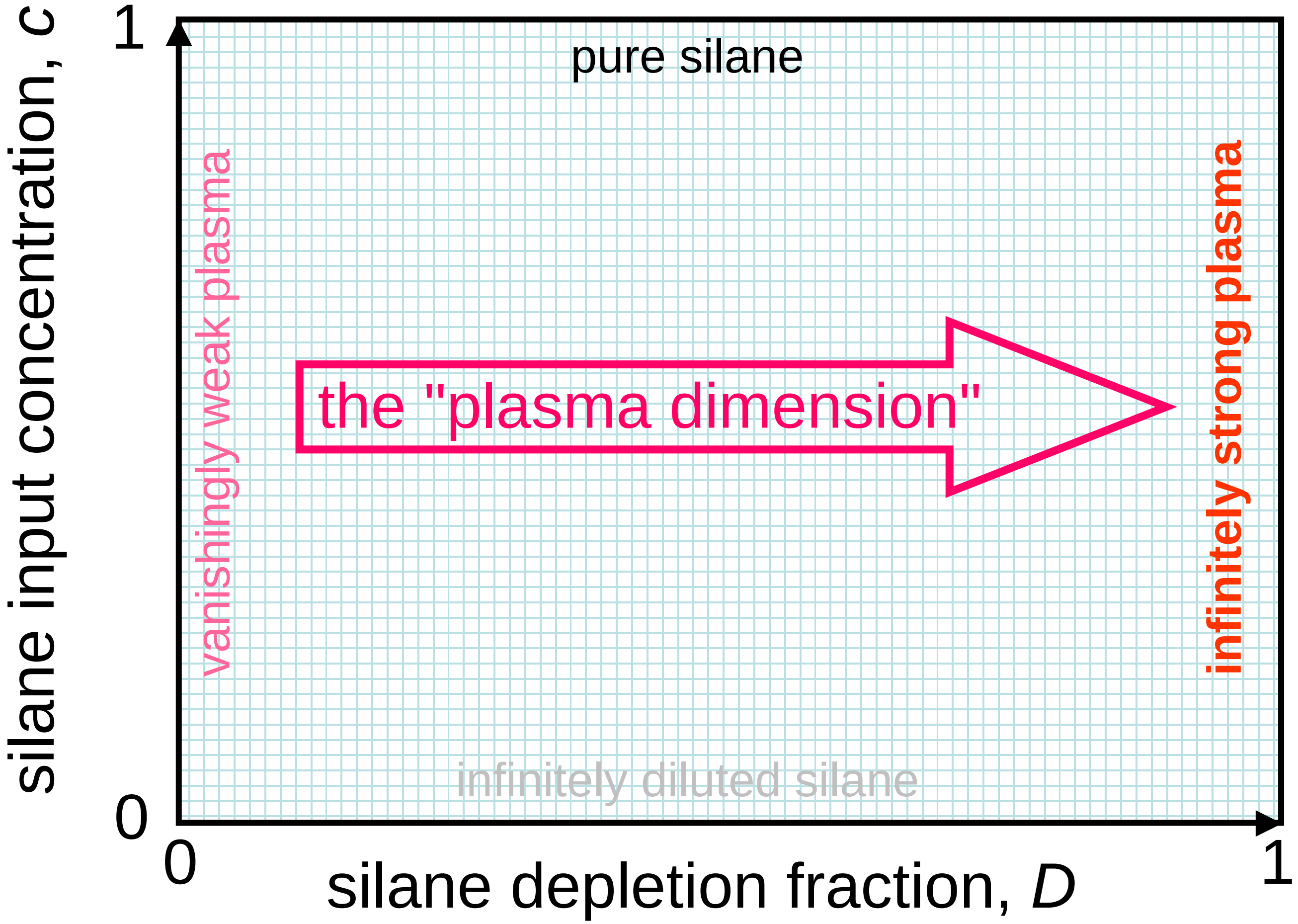
2 parameters, c & D, define the plasma composition

silane fractional depletion, $D = \dfrac{p^0_{SiH_4} - p_{SiH_4}}{p^0_{SiH_4}}$

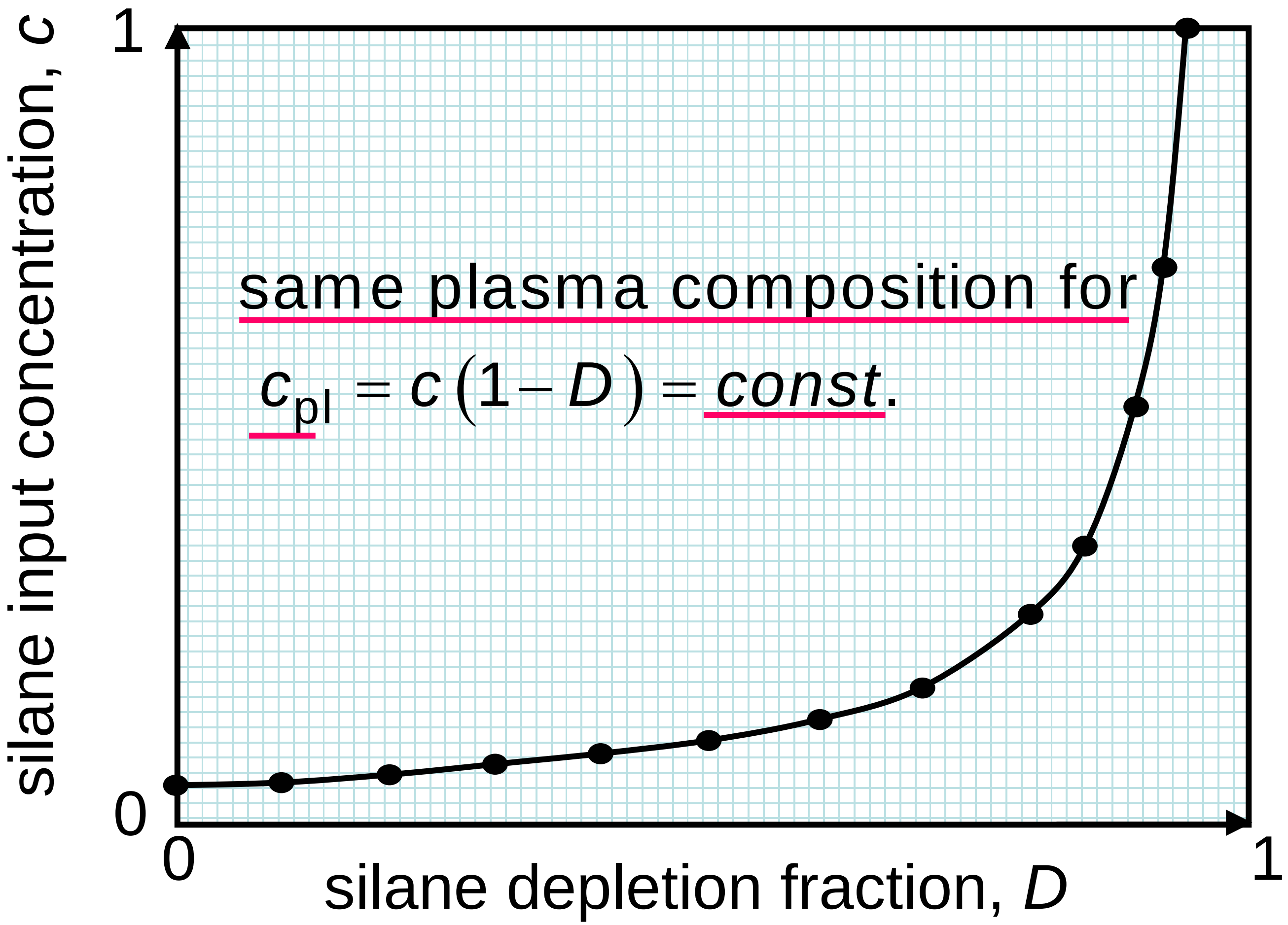
silane concentration with plasma, $c_{pl} = \dfrac{p_{SiH_4}}{p_{process}}$

silane input concentration, $c = \dfrac{p^0_{SiH_4}}{p_{process}}$

The plasma "black box" becomes a {c,D} unit box



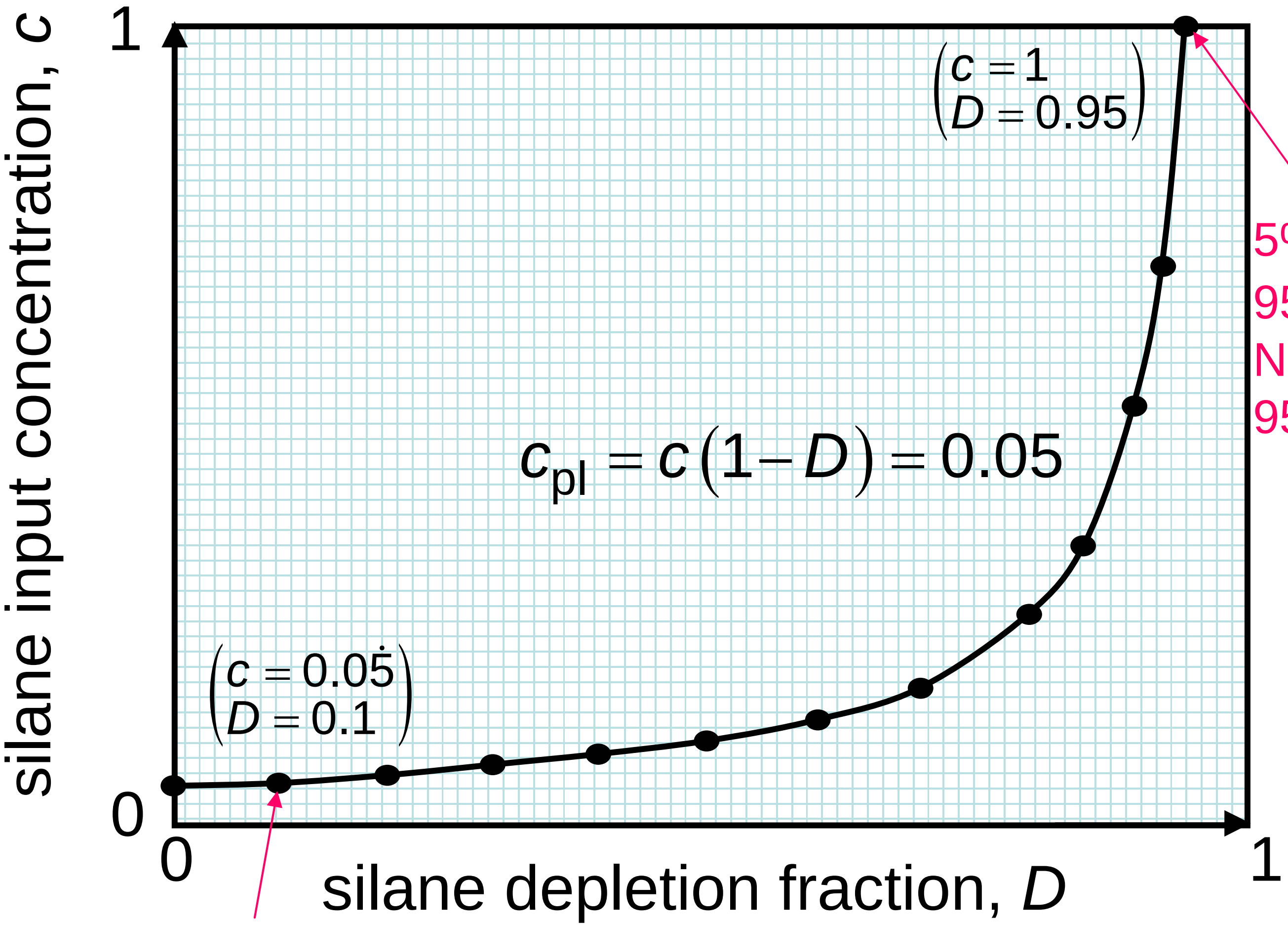
Contours of constant plasma composition



same plasma composition for

$c_{\mathrm{pl}} = c\left(1 - D\right) = const.$

Contours of constant plasma composition



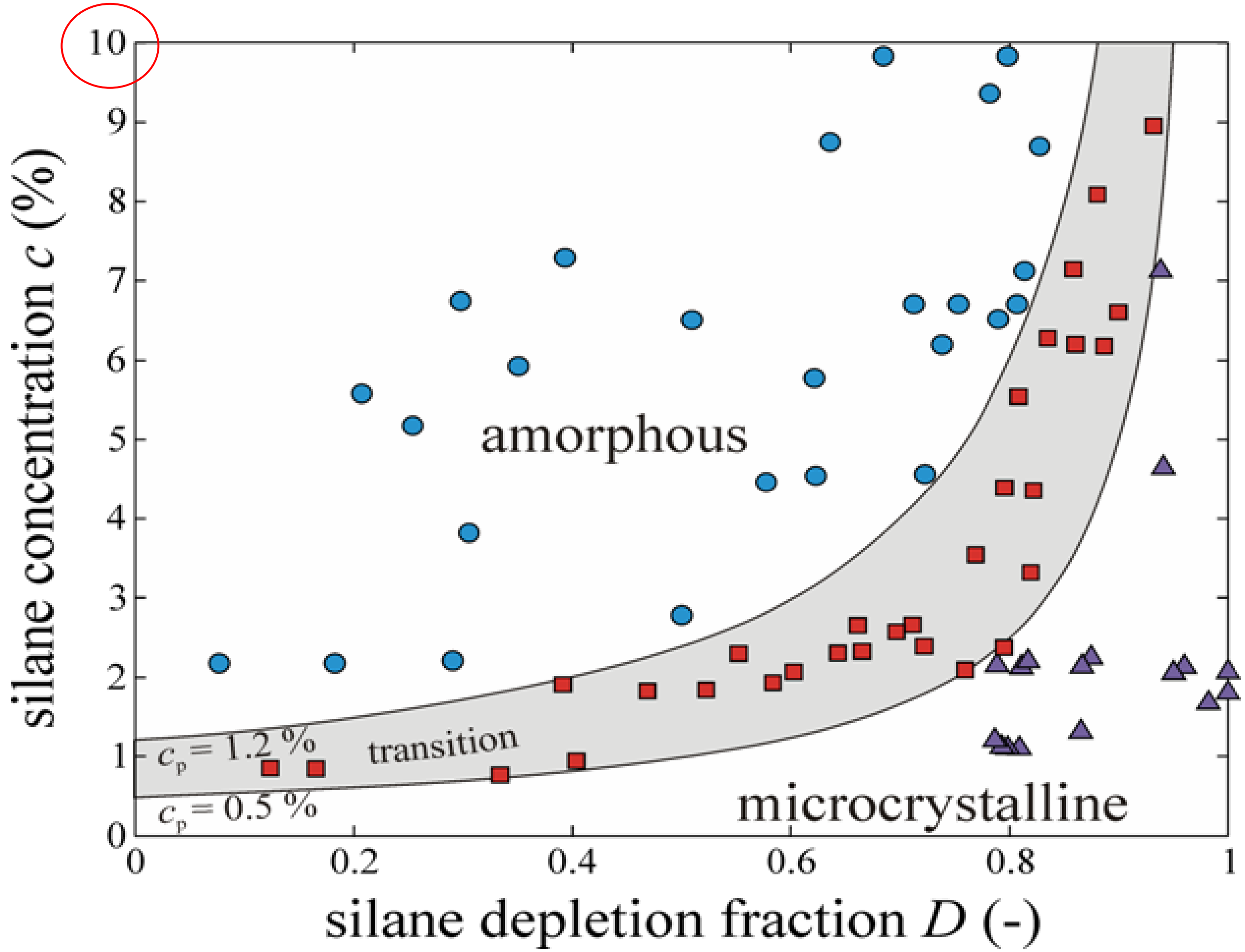
5% silane
95% hydrogen
NO input dilution,
95% depletion

IN THE
PLASMA

5% silane
95% hydrogen
strong input dilution,
weak depletion

IN THE
PLASMA

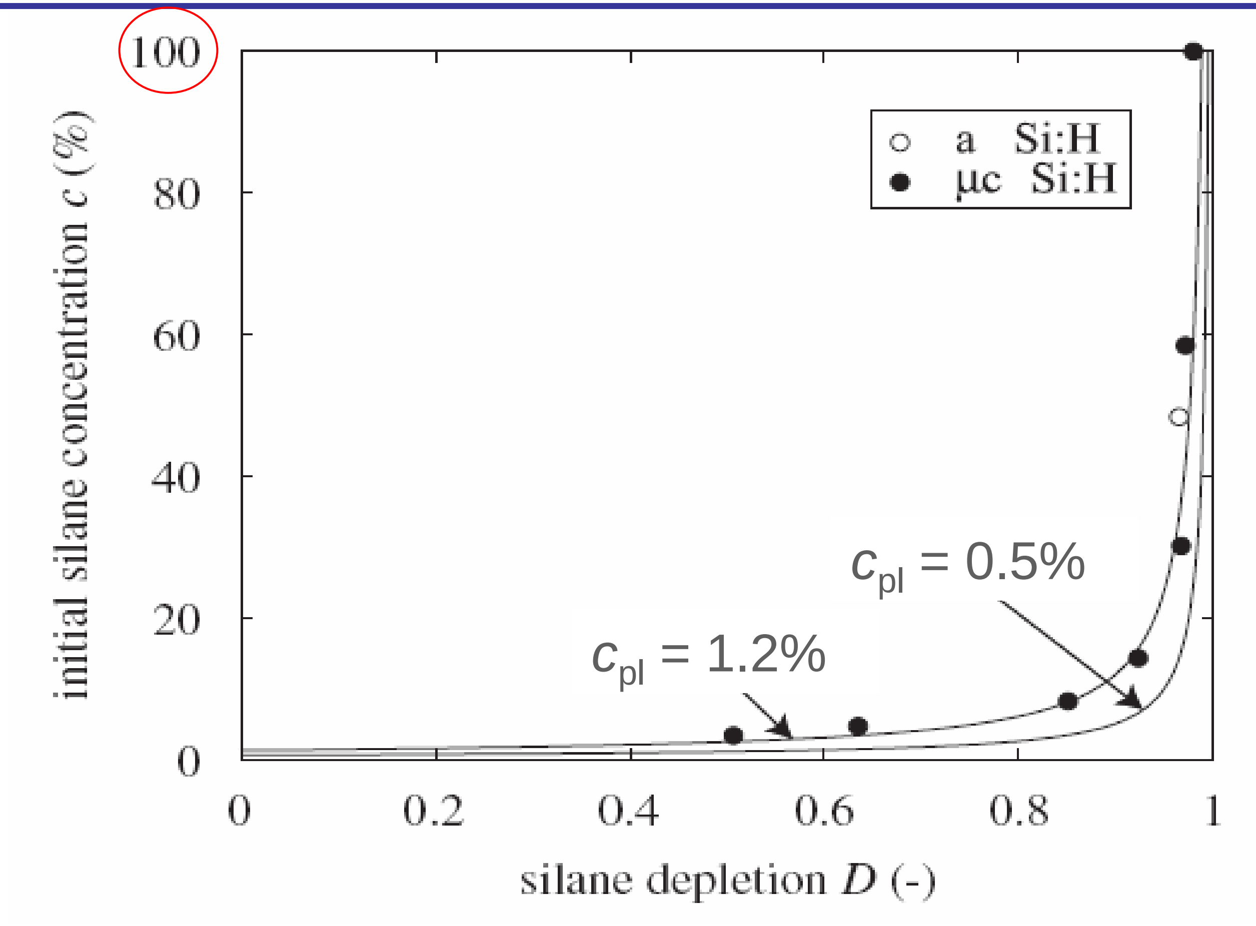
Same plasma composition = same film properties



Constant plasma composition, c_{pl}, gives constant film properties

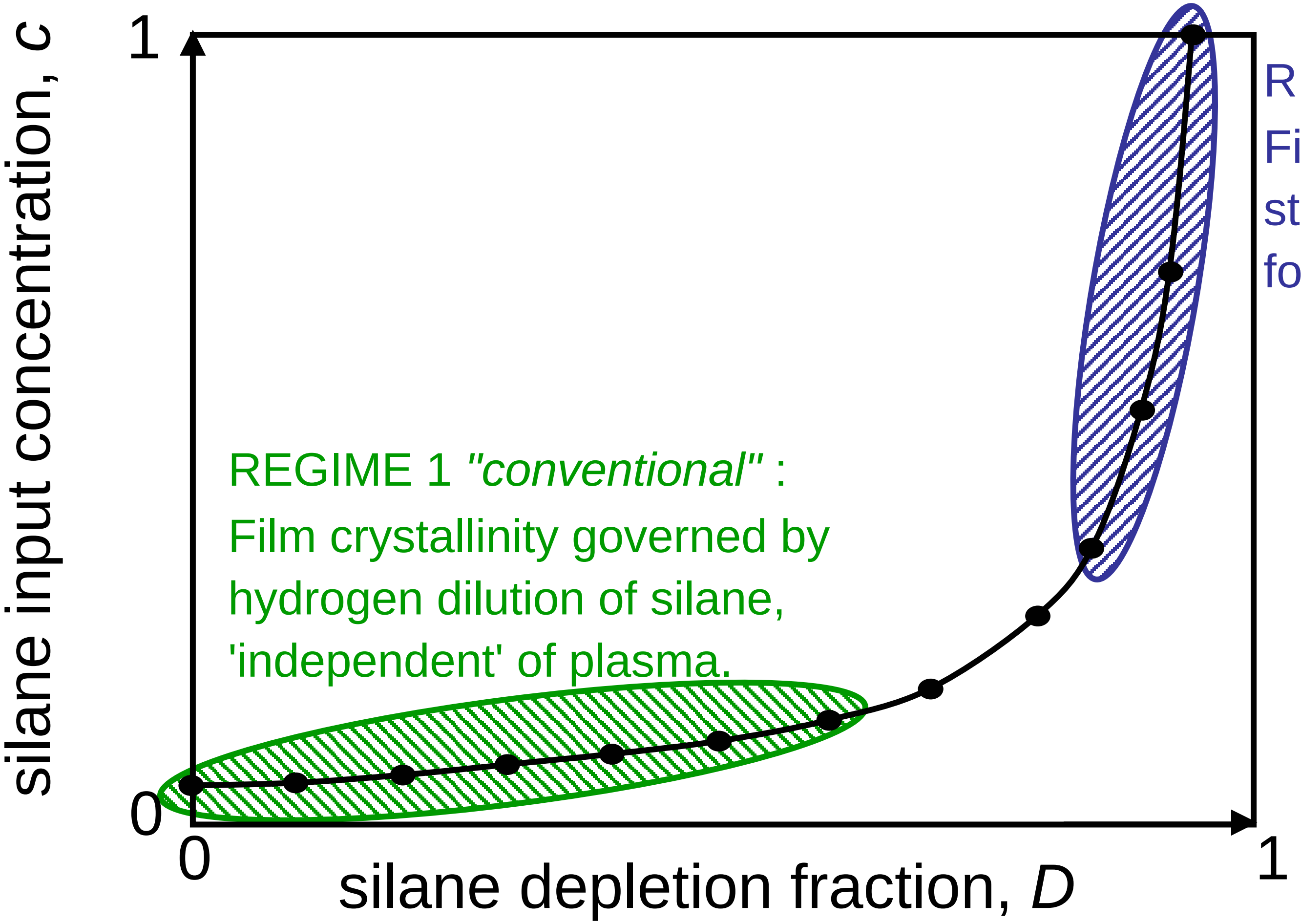
Depletion is an intensive parameter : same depletion gives same plasma conditions

Same plasma composition = same film properties



Microcrystalline silicon can be deposited even with high silane concentration,
provided that the silane depletion fraction is sufficiently high,
because then the plasma is dominated by hydrogen.

Two regimes of operation



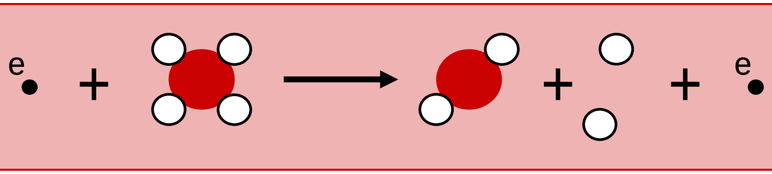
REGIME 2 *"recent"* :
Film crystallinity governed by strong plasma depletion, even for high silane concentration.

REGIME 1 *"conventional"* :
Film crystallinity governed by hydrogen dilution of silane, 'independent' of plasma.

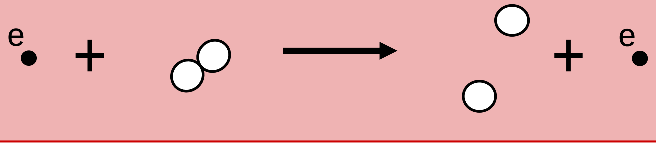
Simple plasma chemistry model

Based on a reduced set of gas phase reactions…

$$e + SiH_4 \xrightarrow{k_1} SiH_2 + 2H + e$$

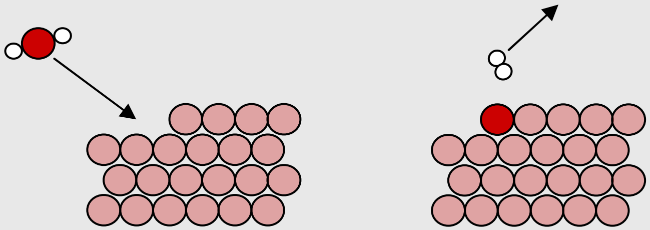


$$e + H_2 \xrightarrow{k_H} 2H + e$$

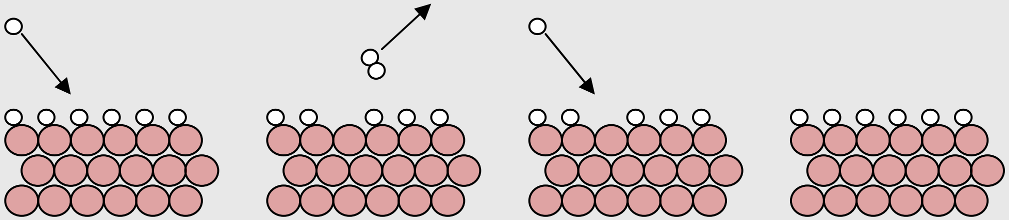


…and simplified, multi-step, surface reactions.

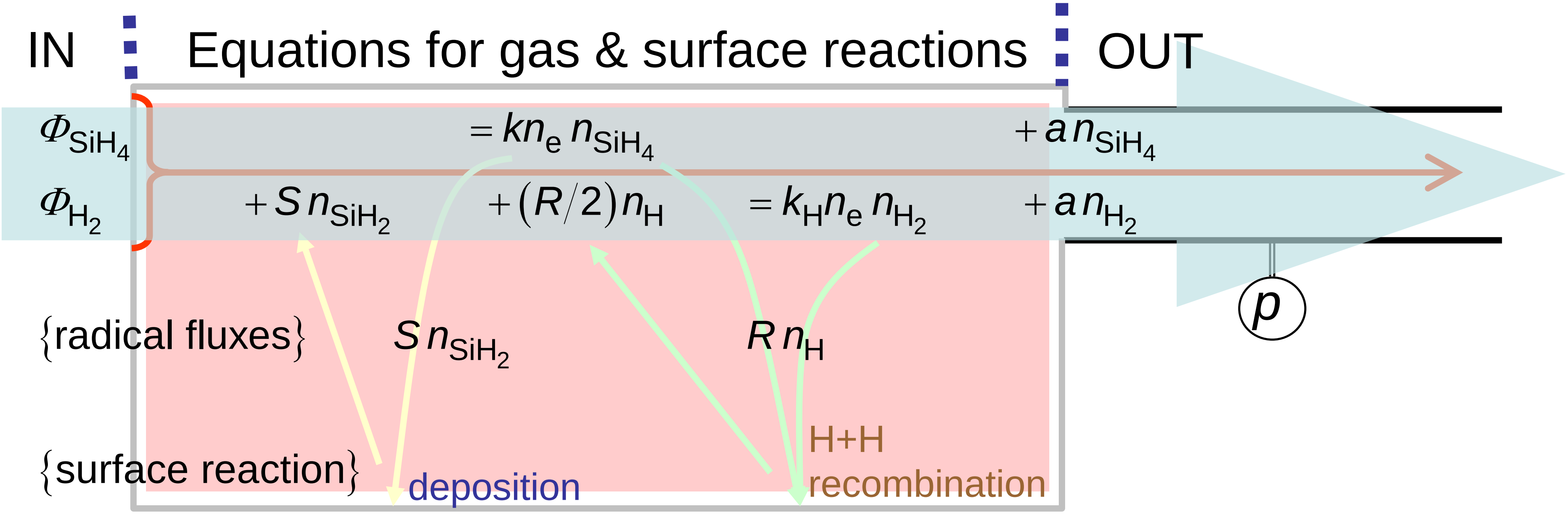
$$SiH_2 \xrightarrow{S} Si_{surf} + H_2$$



$$\begin{array}{l} H + H_{surf} \longrightarrow H_2 + \text{vacancy} \\ H + \text{vacancy} \longrightarrow H_{surf} \qquad + \\ \hline H \xrightarrow{R} \frac{1}{2} H_2 \end{array}$$



Simple, analytical plasma chemistry model



$$\Phi_{SiH_4} = k n_e n_{SiH_4} + a n_{SiH_4}$$

$$\Phi_{H_2} + S n_{SiH_2} + (R/2) n_H = k_H n_e n_{H_2} + a n_{H_2}$$

- A zero-dimensional model can be appropriate to showerhead reactors (see section I)
- *"a"* is the inverse residence time, an effective "pumping speed"

0-dimensional model; first order reaction rate balance for each species.

flow in

lost by electron impact dissociation

inverse residence time (pumping loss)

$$\mathrm{SiH_4}: \; \Phi_{\mathrm{SiH_4}} - (k n_{\mathrm{e}} + a) n_{\mathrm{SiH_4}} = 0$$

produced by dissocation

lost by deposition

$$\mathrm{SiH_2}: \; k n_{\mathrm{e}} n_{\mathrm{SiH_4}} - S n_{\mathrm{SiH_2}} = 0$$

flow in

produced by surface association

produced during deposition

lost by dissocation

inverse residence time (pumping loss)

$$\mathrm{H_2}: \; \Phi_{\mathrm{H_2}} + \frac{1}{2} R n_{\mathrm{H}} + S n_{\mathrm{SiH_2}} - (k_{\mathrm{H}} n_{\mathrm{e}} + a) n_{\mathrm{H_2}} = 0$$

$$\mathrm{H}: \; 2 k n_{\mathrm{e}} n_{\mathrm{SiH_4}} + 2 k_{\mathrm{H}} n_{\mathrm{e}} n_{\mathrm{H_2}} - R n_{\mathrm{H}} = 0$$

produced by dissocation of silane

produced by dissocation of hydrogen

loss rate by surface association

B. Strahm, A. A. Howling, L. Sansonnens and Ch. Hollenstein, *Plasma Sources Sci. Technol.* **16**, 80 (2007).

Simple, analytical plasma chemistry model

- Just one silane dissociation channel here: $e + SiH_4 \longrightarrow SiH_2 + 2H + e$
- More detailed plasma chemistry only changes the numerical constants:
- ... the general conclusions remain the same.

$$\boxed{\text{radical flux ratio} \quad \frac{\Gamma_{H}}{\Gamma_{SiH_2}}} = \frac{R n_{H}}{S n_{SiH_2}} = 2\frac{k_{H}}{k}\left(\frac{n_{H_2}}{n_{SiH_4}}\right) + 2 = 2\frac{k_{H}}{k}\left(\frac{1}{c_{pl}} - 1\right) + 2$$

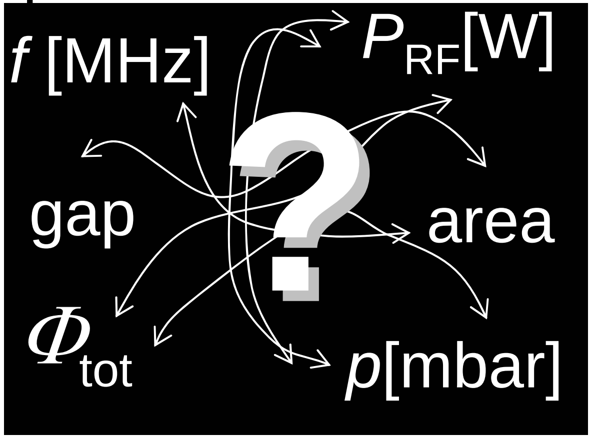
Hydrogen and silane are the dominant partial pressures;

so we can expect radical densities to depend on them.

"This shows why the plasma deposition is determined by c_{pl} ,
the silane concentration ***in the plasma.***"

Depletion accounts for many of the plasma parameters

plasma black box



analytical model

all of these are *intensive* parameters

$$D = \left(1 + \frac{a/kn_e}{(1+c)}\right)^{-1}$$

$$a\left[\mathrm{s}^{-1}\right] = \text{ inverse residence time } = \text{ effective pumping speed } = 6.1 \cdot 10^{-6}\,\frac{T_{gas}\Phi_{total}}{p \cdot \mathrm{gap} \cdot \mathrm{area}};$$

$$kn_e\left[\mathrm{s}^{-1}\right] = \text{ silane dissociation rate } = \text{ plasma dissociation frequency} = F\left(P_{RF},\ f\,[\mathrm{MHz}]\right);$$

$$c = \text{ silane input concentration, } \frac{\Phi_{SiH_4}}{\Phi_{total}}.$$

Depletion scaling:

$$D\uparrow \text{ if any of } \{p,\ \mathrm{gap},\ \mathrm{area},\ c,\ P_{RF},\ f\}\uparrow \text{ \&/or } \{\Phi_{total},\ T_{gas}\}\downarrow$$

Intermediate Conclusions

- Plasma composition and deposition depend on the silane concentration in the plasma, $c_{pl}=c(1-D)$, *and not only* on the silane concentration in the input flow, c.

Strong hydrogen dilution in the plasma, and μc-Si:H deposition, can be obtained with high input concentration of silane and strong depletion.

- The fractional depletion of silane, D, is an *intensive* parameter.

Depletion measurement could be a useful diagnostic check for the same plasma conditions in the transfer of process parameters to an upscaled reactor. Monitored non-intrusively by infrared absorption spectroscopy in the pumping line.

- A zero-dimensional model, appropriate for a uniform large-area reactor, can be used to estimate the relation between intensive plasma parameters.

Refs. B. Strahm, A. A. Howling, L. Sansonnens and Ch. Hollenstein, *Plasma Sources Sci. Technol.* **16**, 80 (2007).

A. A. Howling, B. Strahm and Ch. Hollenstein, *Thin Solid Films* (2009), doi:10.1016/j.tsf.2009.02.053

R. Bartlome, A. Feltrin and Ch. Ballif, *Appl. Phys. Lett.* **94**, 201501 (2009) - Quantum Cascade Laser