Plasma modelling & reactor design

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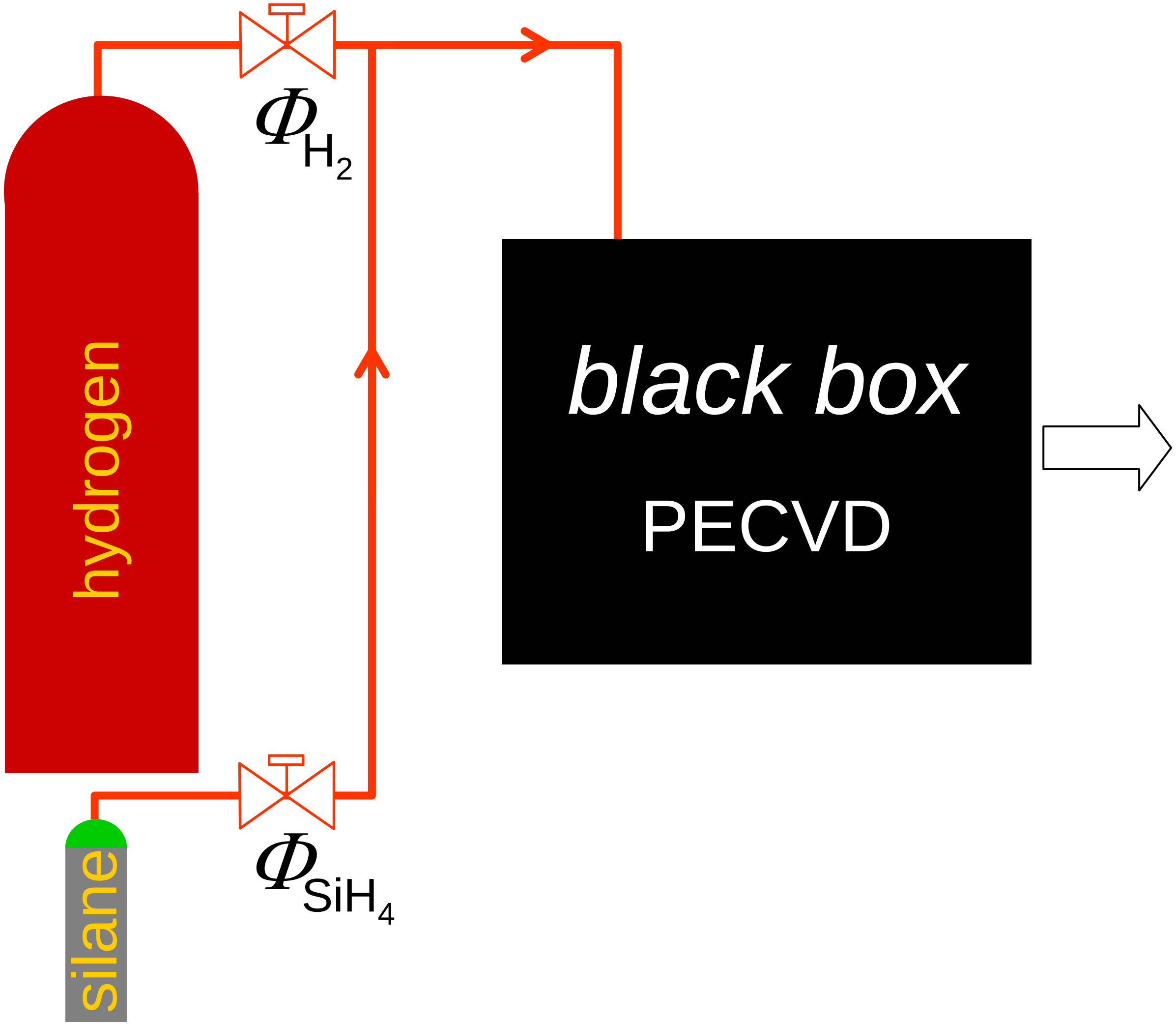
1) The "plasma dimension" for plasma deposition of μc-Si:H
2) Direct pumping of a plasma reactor

... and one non-intrusive plasma diagnostic for each.

1) Plasma-Enhanced Chemical Vapour Deposition of μc-Si:H



hydrogen

Φ_{H_2}

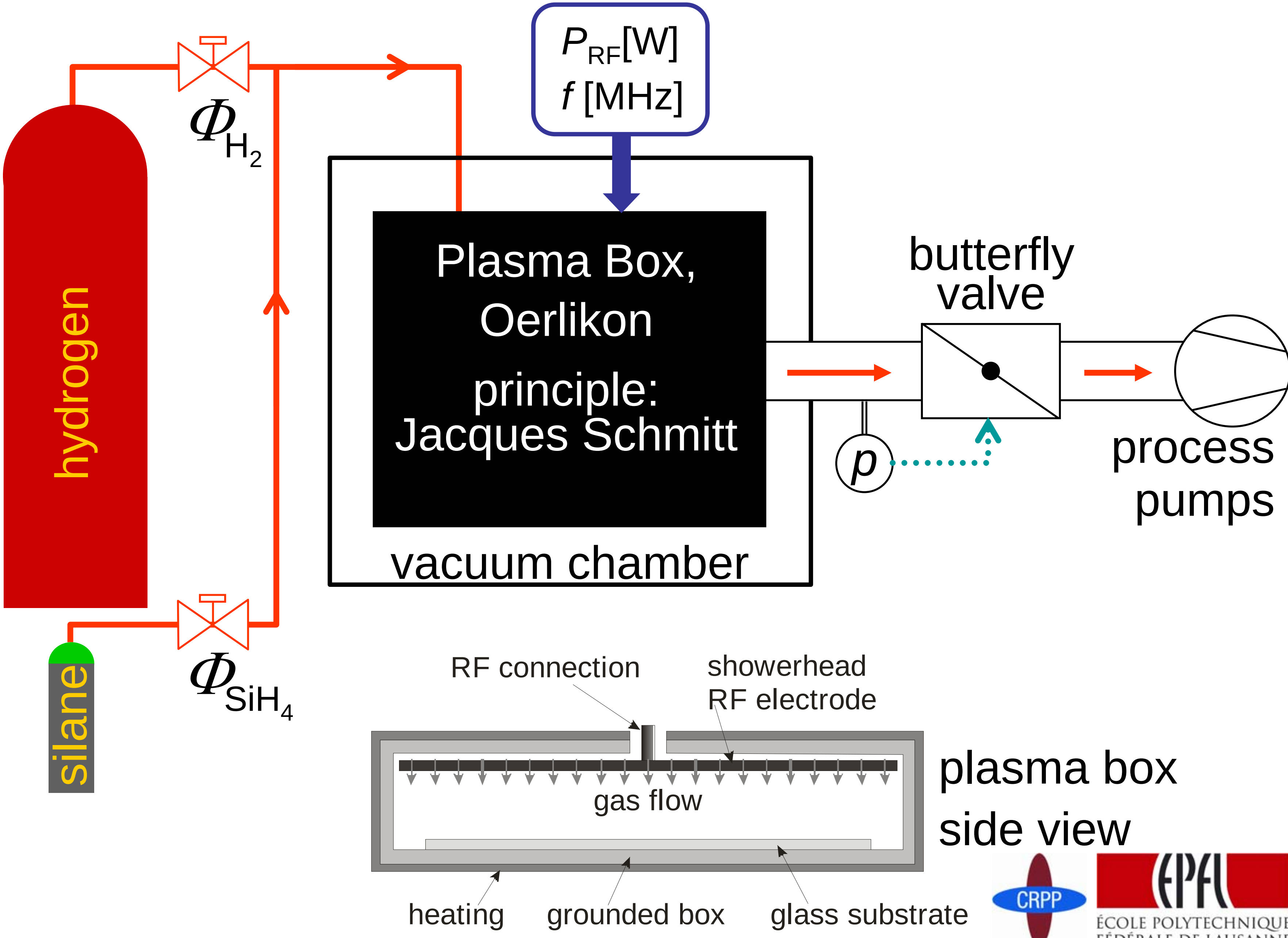
silane

Φ_{SiH_4}

black box

PECVD

1) PECVD reactor setup



P_{RF}[W]
f [MHz]

Plasma Box, Oerlikon

principle: Jacques Schmitt

vacuum chamber

butterfly valve

process pumps

p

hydrogen

silane

Φ_{H_2}

Φ_{SiH_4}

RF connection

showerhead RF electrode

gas flow

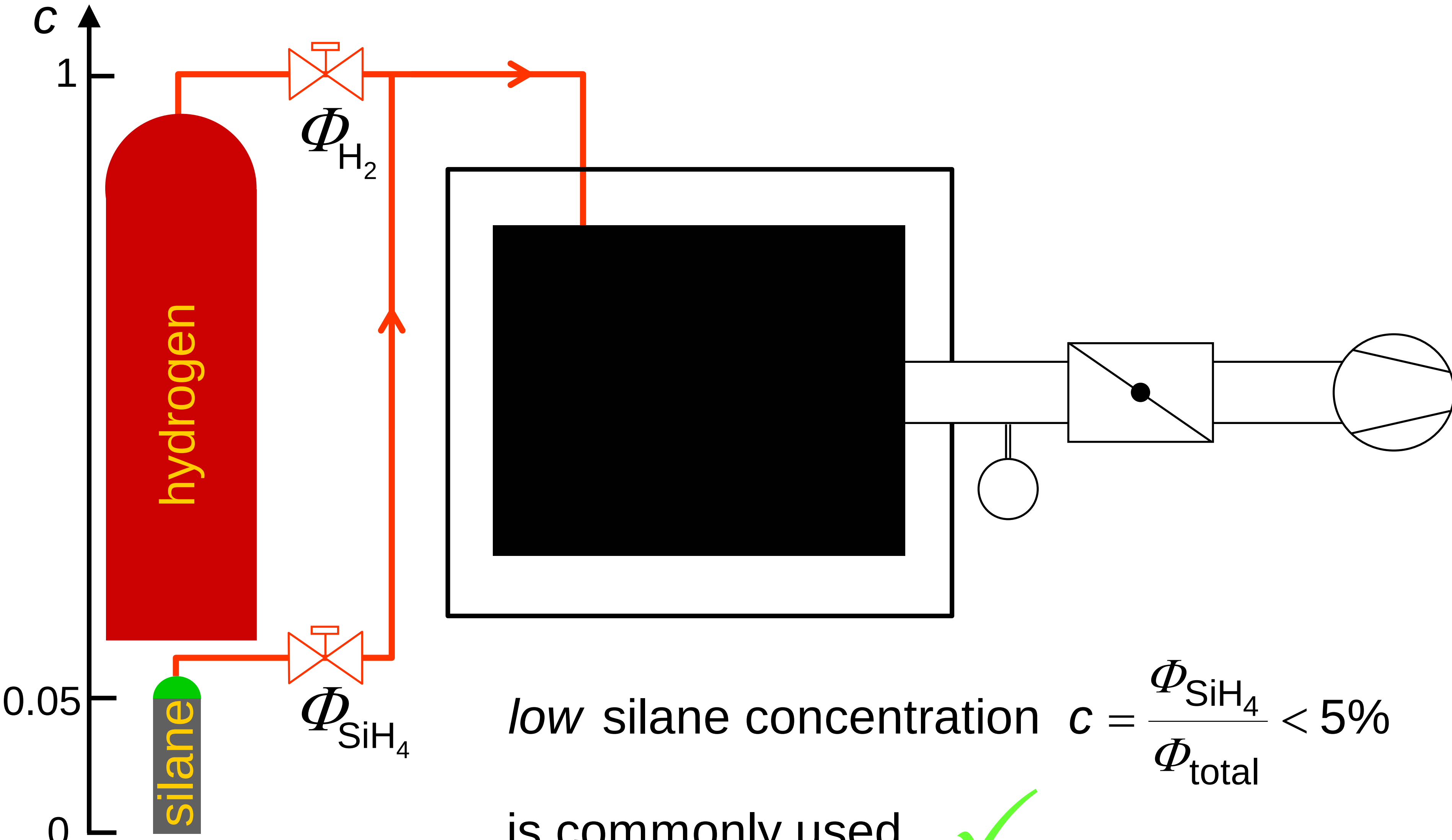
heating

grounded box

glass substrate

plasma box side view

1) Hydrogen dilution for plasma deposition of μc-Si:H



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

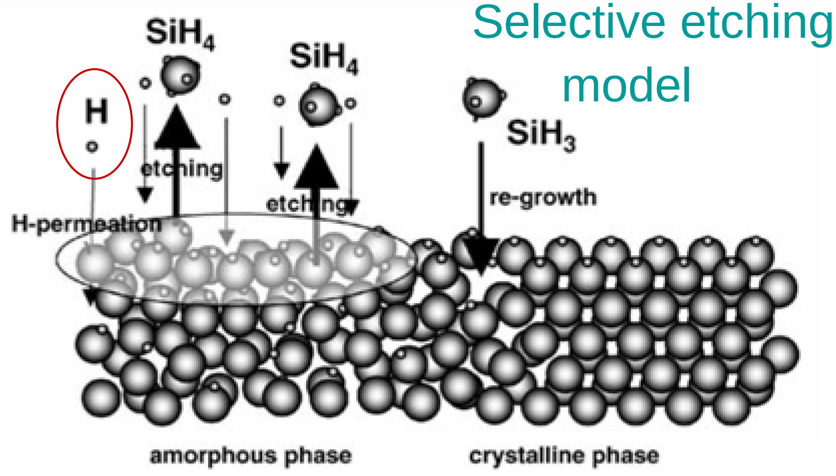
is commonly used ✓

1) Reason for hydrogen dilution

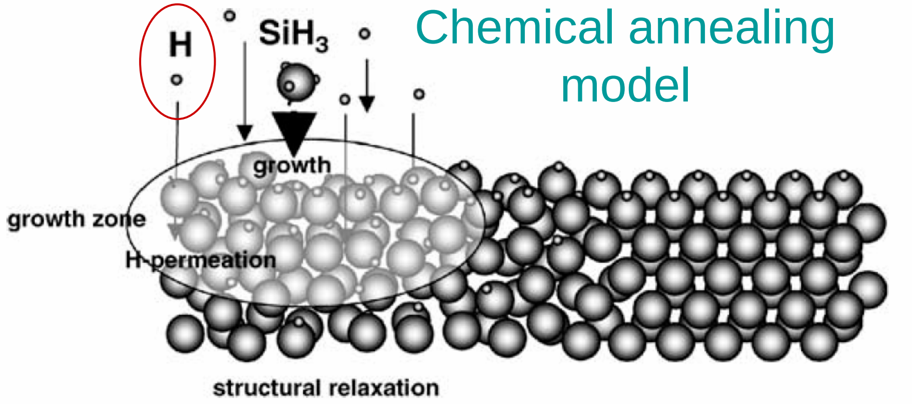
Need high ratio of
H to SiH_x fluxes
to deposit μc-Si:H

intuitively

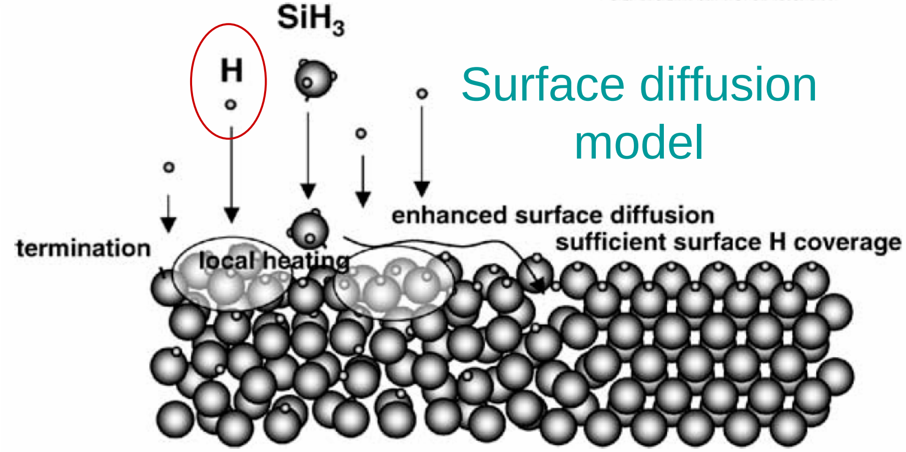
"Add more hydrogen
than silane"



Selective etching
model

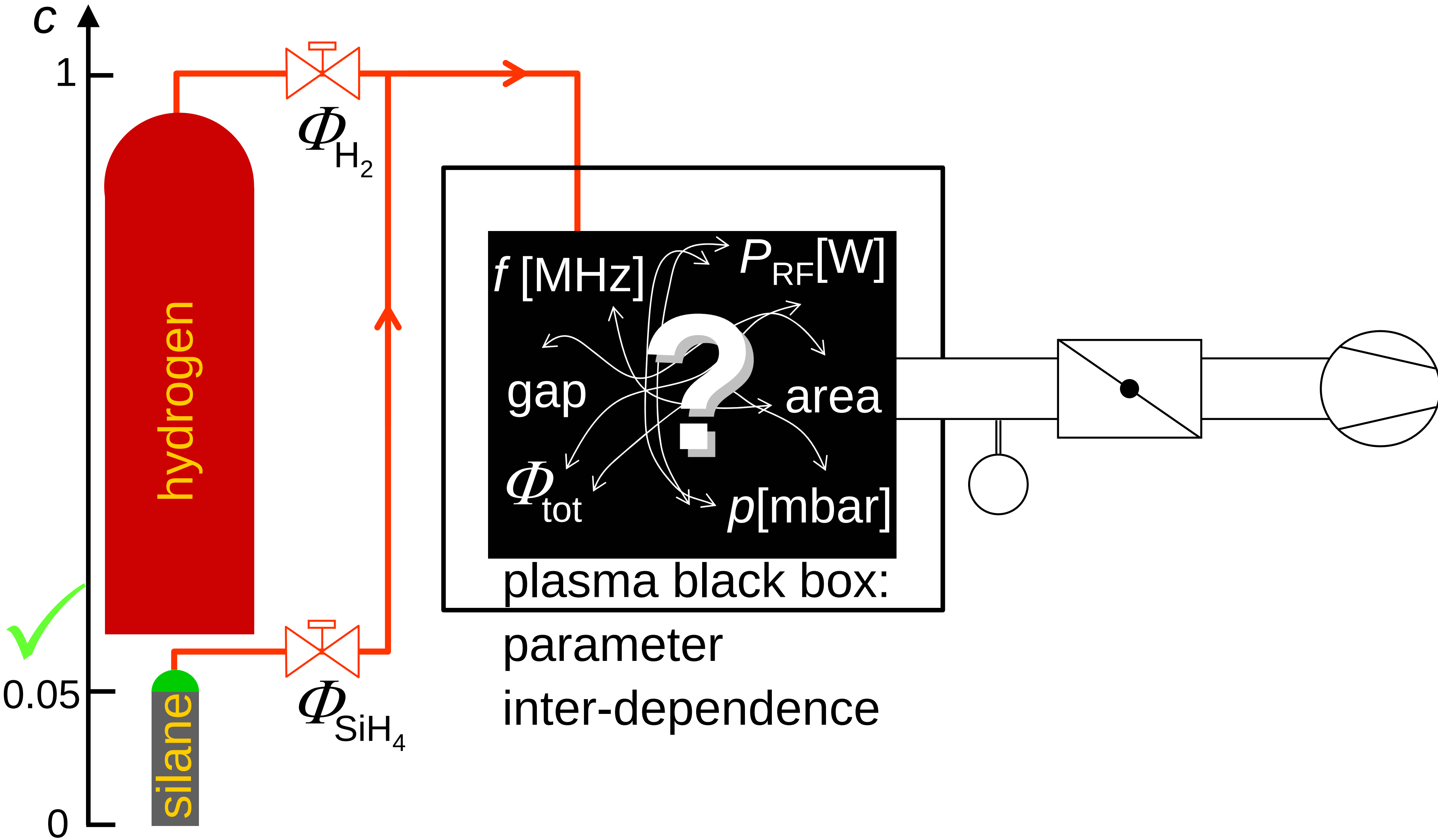


Chemical annealing
model



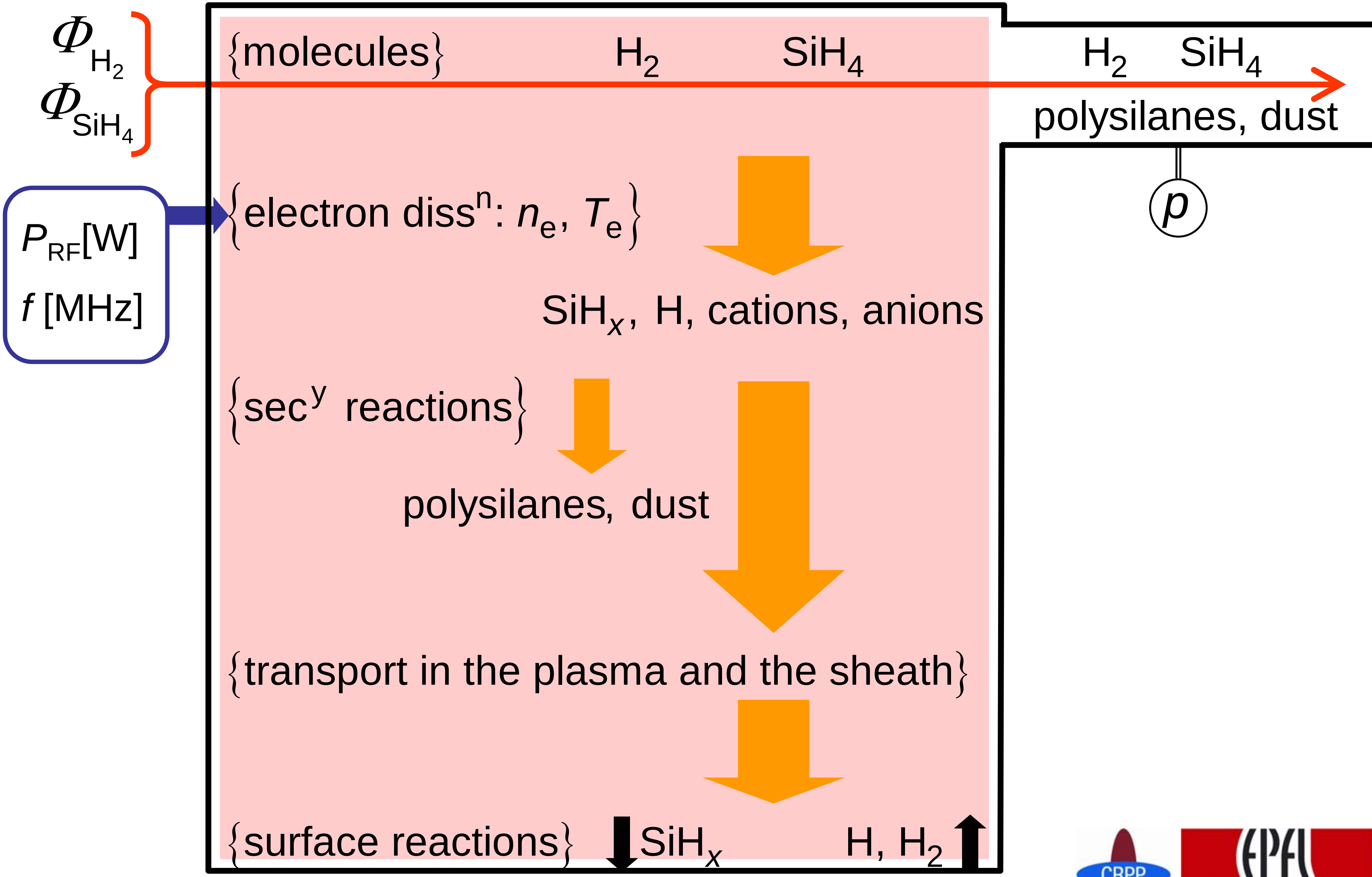
Surface diffusion
model

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



plasma black box:
parameter
inter-dependence

1) ...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

{electron dissⁿ: n_e, T_e}

SiH_x, H, cations, anions

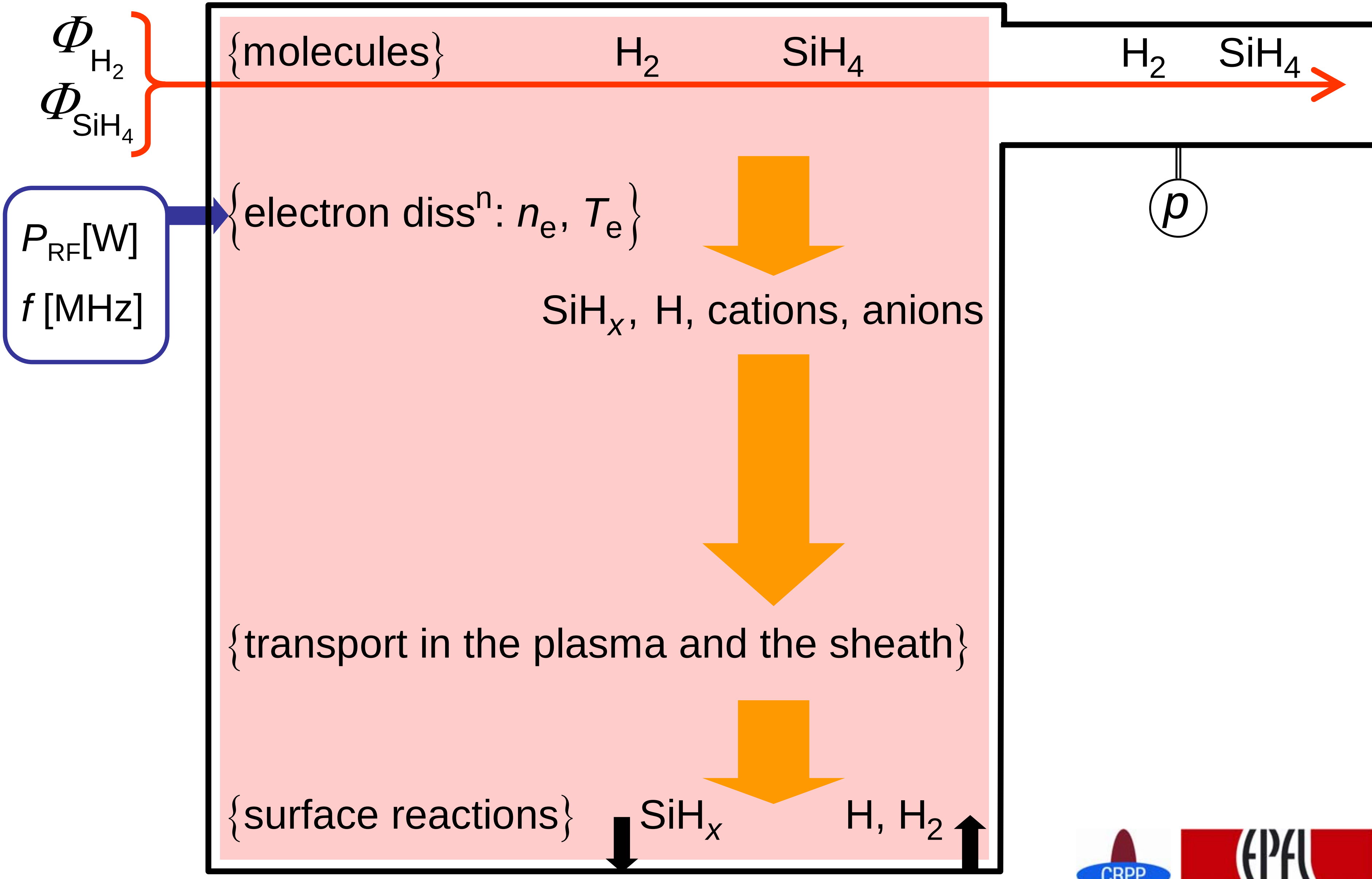
{sec^y reactions}

polysilanes, dust

{transport in the plasma and the sheath}

{surface reactions} SiH_x H, H_2

1) Consider low pressures (< 2 mbar)



Φ_{H_2}

Φ_{SiH_4}

P_{RF}[W]

f [MHz]

{molecules} H_2 SiH_4

H_2 SiH_4

p

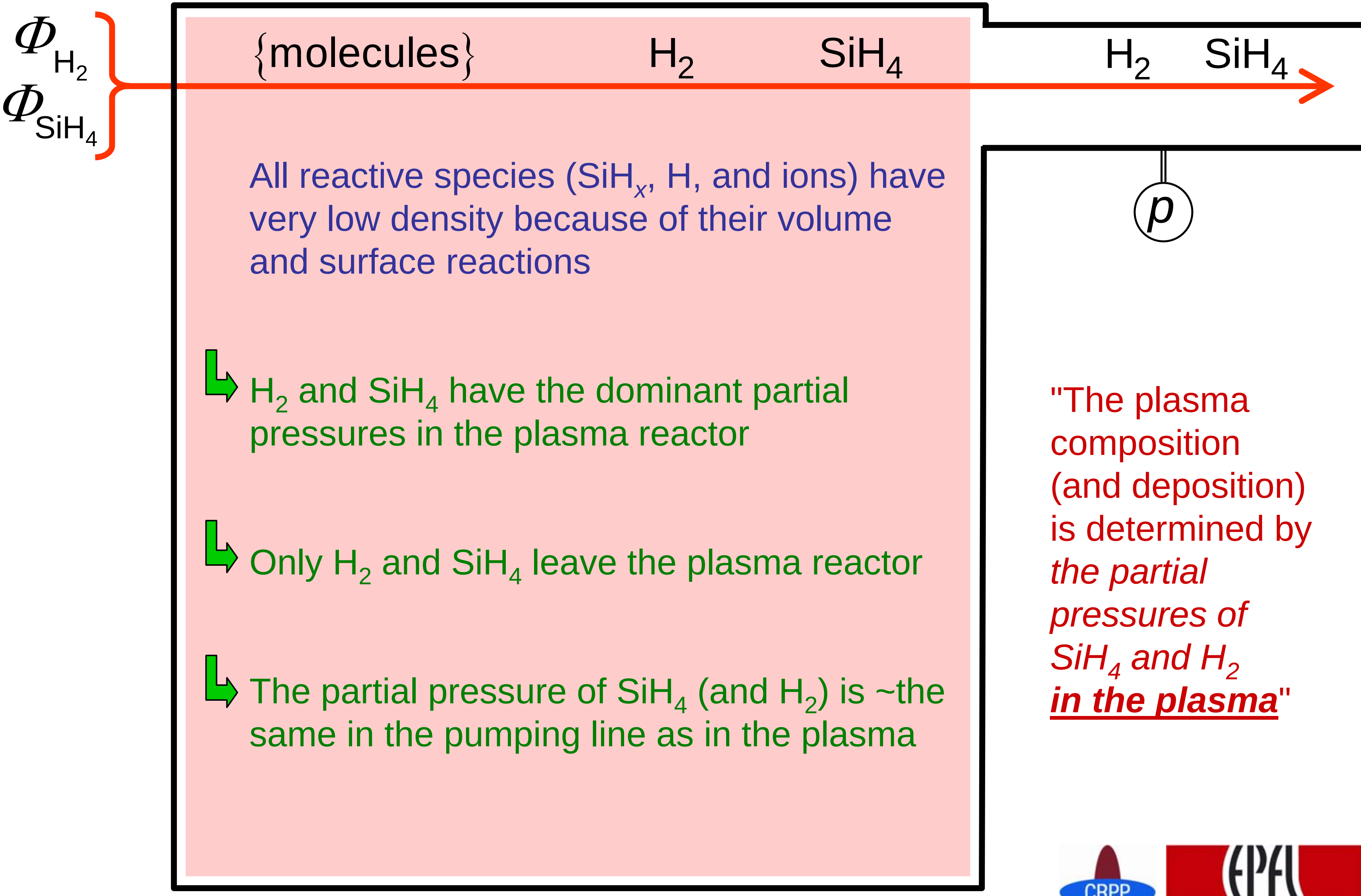
{electron diss^n: n_e, T_e}

SiH_x, H, cations, anions

{transport in the plasma and the sheath}

{surface reactions} SiH_x H, H_2

1) 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

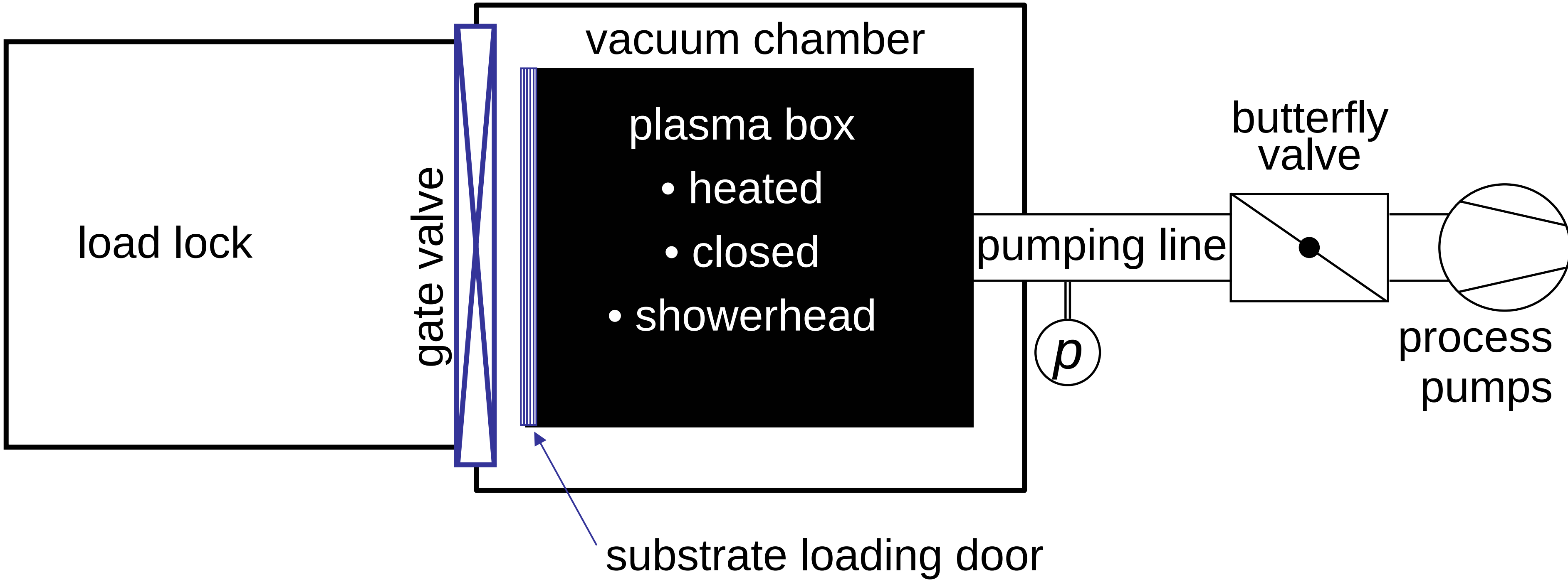
↳ Only H_2 and SiH_4 leave the plasma reactor

↳ The partial pressure of SiH_4 (and H_2) is ~the same in the pumping line as in the plasma

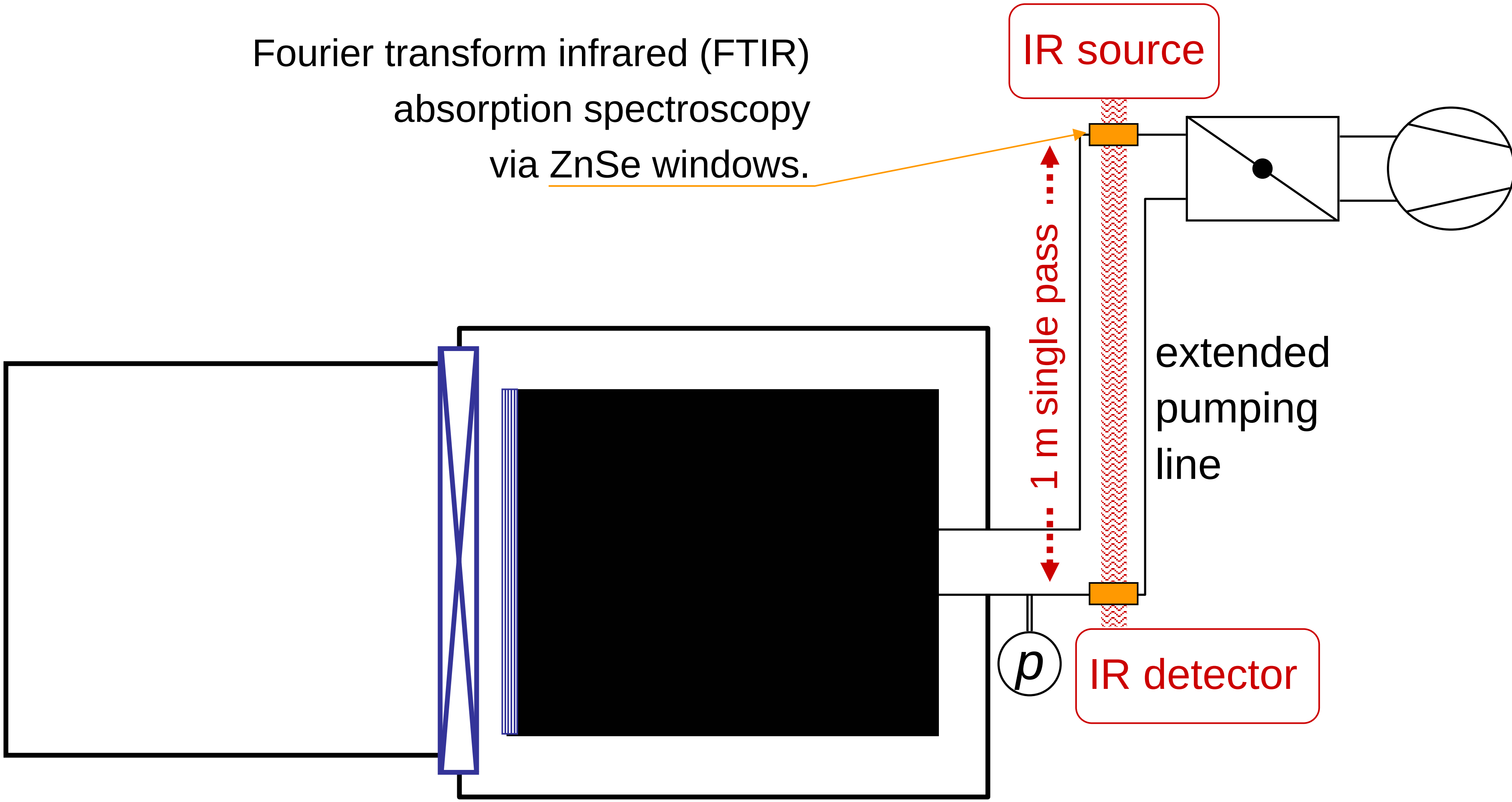
"The plasma composition (and deposition) is determined by *the partial pressures of SiH_4 and H_2* ***<u>in the plasma</u>***"

1) How to measure the silane partial pressure in the plasma?

"inaccessible" plasma reactor



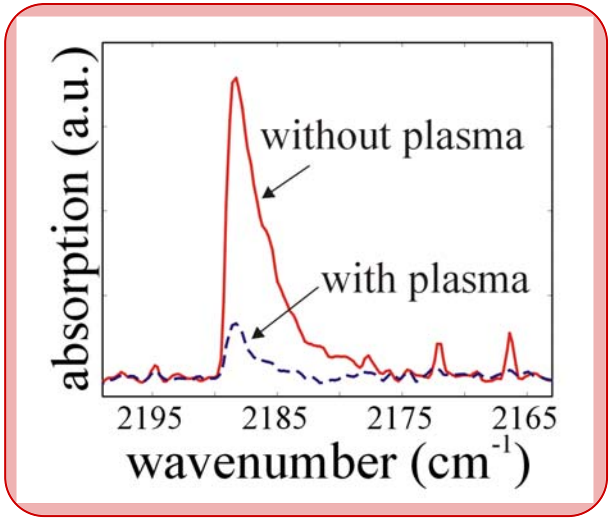
1) FTIR in pump line: Non-intrusive diagnostic for SiH_4 pressure

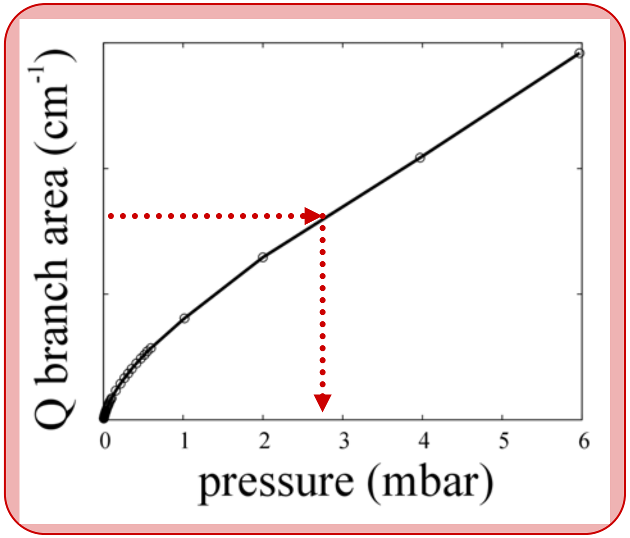


Fourier transform infrared (FTIR)
absorption spectroscopy
via ZnSe windows.

1) Silane partial pressure measurement

a) Silane Q-branch absorbance; *b)* Integrate spectrum; *c)* Read off a calibrated curve





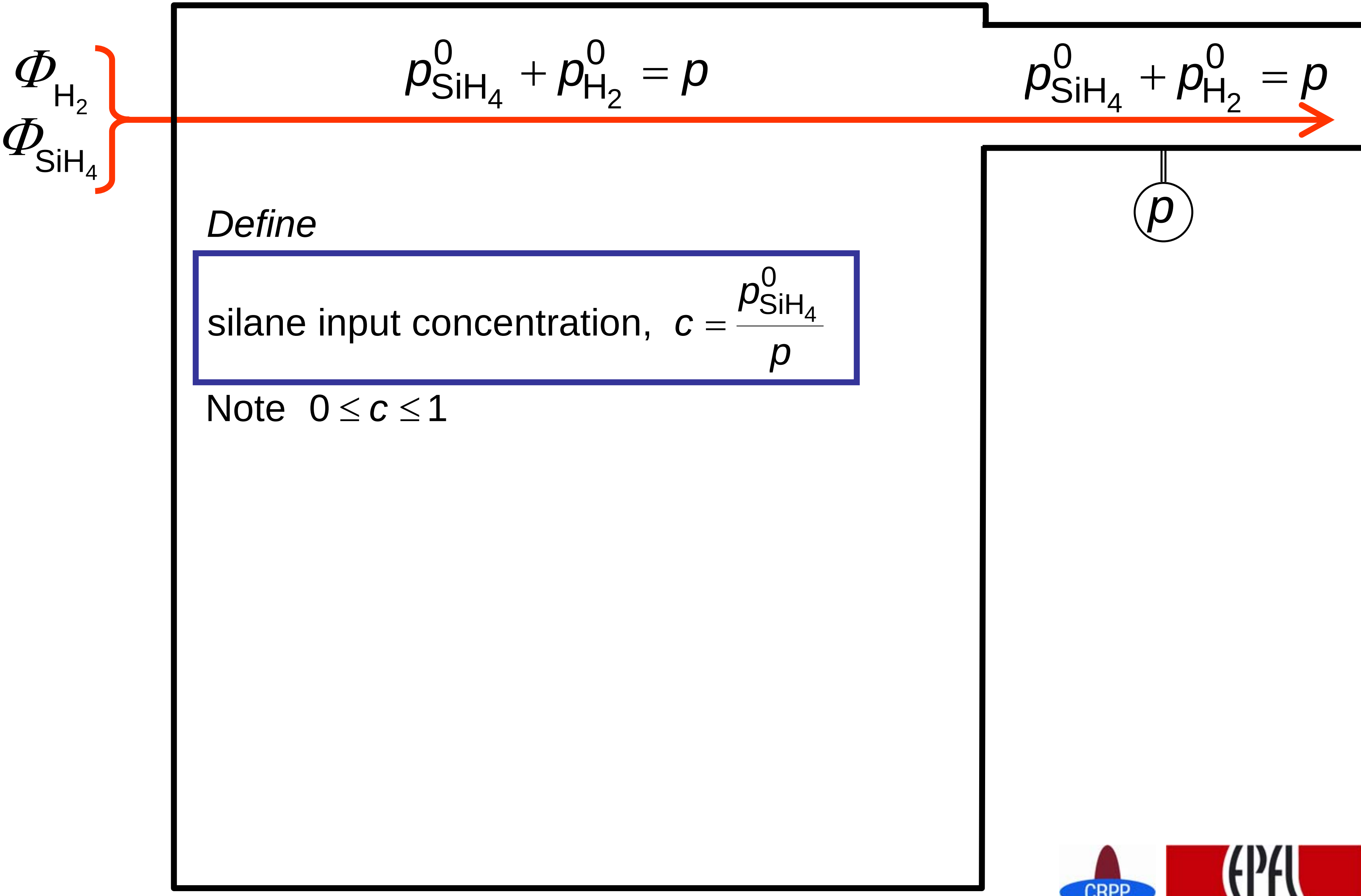
- Silane pressure with plasma < silane pressure without plasma,

$$\boxed{p_{SiH_4} < p^0_{SiH_4}} ,$$

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

- Hydrogen partial pressure increases with plasma (surface recombination, & pump speed adjustment)

1) Silane input concentration (*without* plasma)



Φ_{H_2}
Φ_{SiH_4}

$$p^0_{SiH_4} + p^0_{H_2} = p$$

$$p^0_{SiH_4} + p^0_{H_2} = p$$

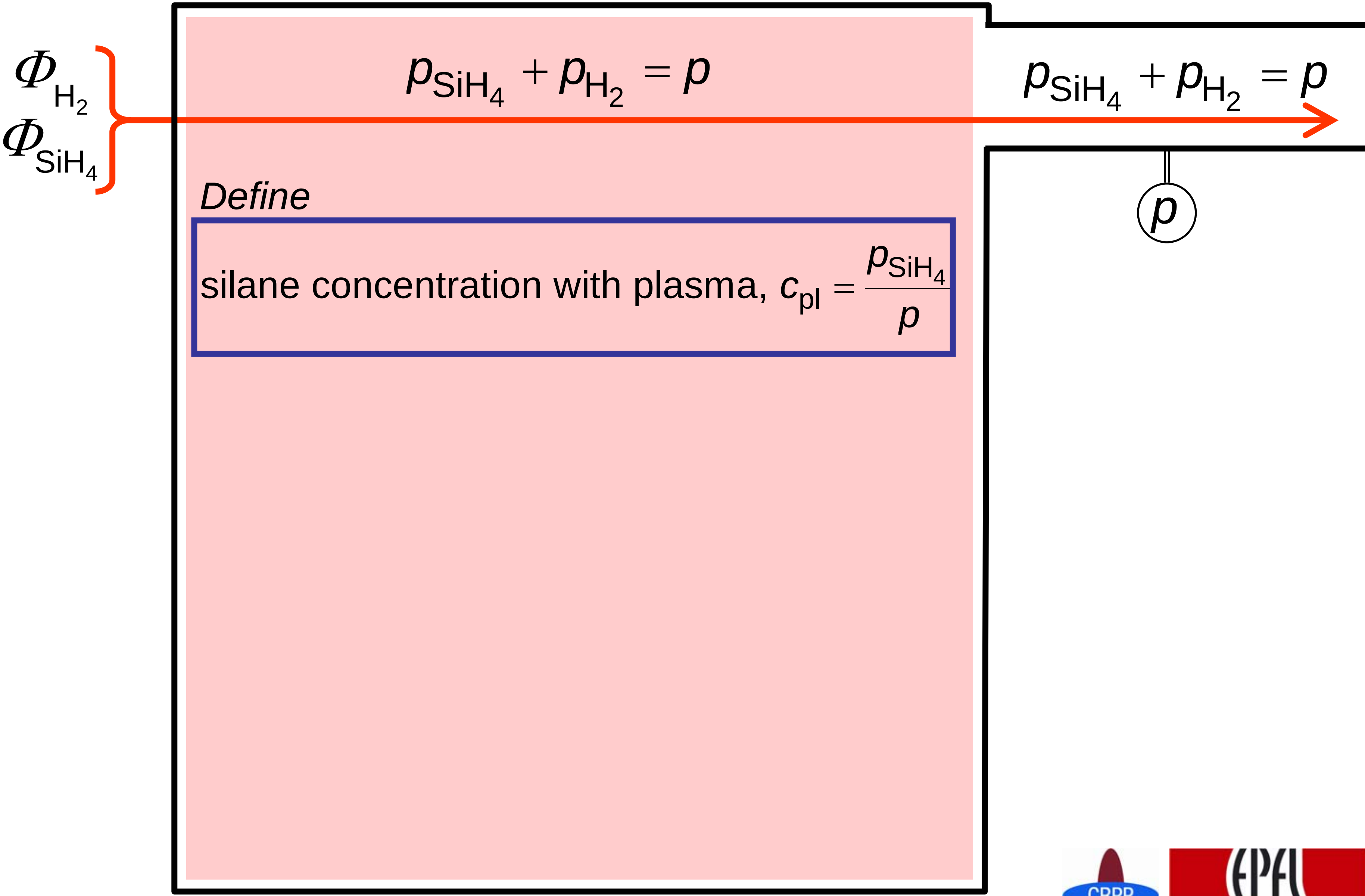
p

Define

$$\boxed{\text{silane input concentration,}\quad c = \frac{p^0_{SiH_4}}{p}}$$

Note $0 \le c \le 1$

1) Silane concentration *with* plasma



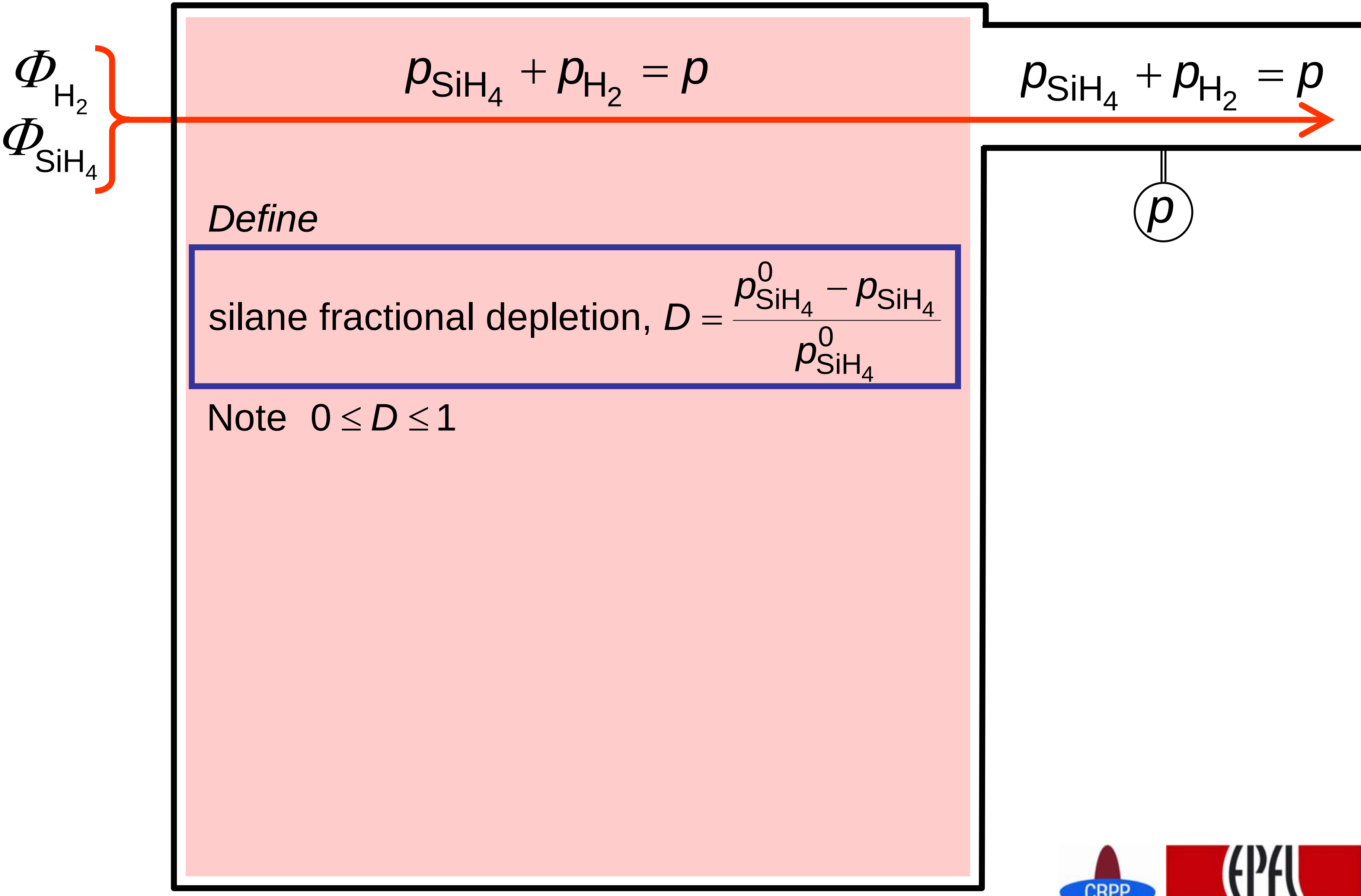
$$p_{SiH_4} + p_{H_2} = p$$

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

Define

silane concentration with plasma, $c_{pl} = \frac{p_{SiH_4}}{p}$

1) Silane depletion due to plasma



Φ_{H_2}

Φ_{SiH_4}

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

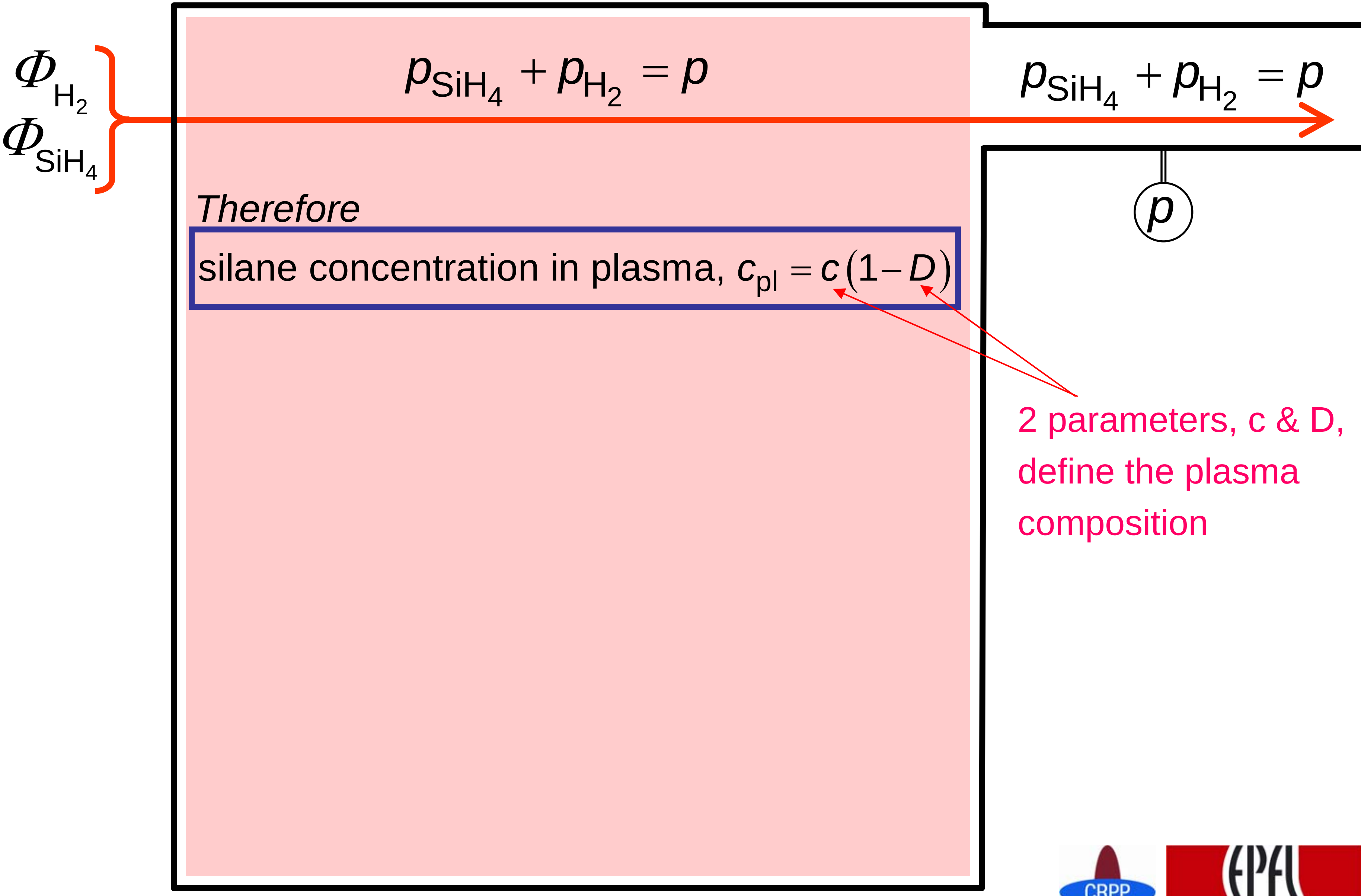
$$p_{SiH_4} + p_{H_2} = p$$

Define

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

Note $0 \le D \le 1$

1) Silane concentration in plasma



Φ_{H_2}

Φ_{SiH_4}

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

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

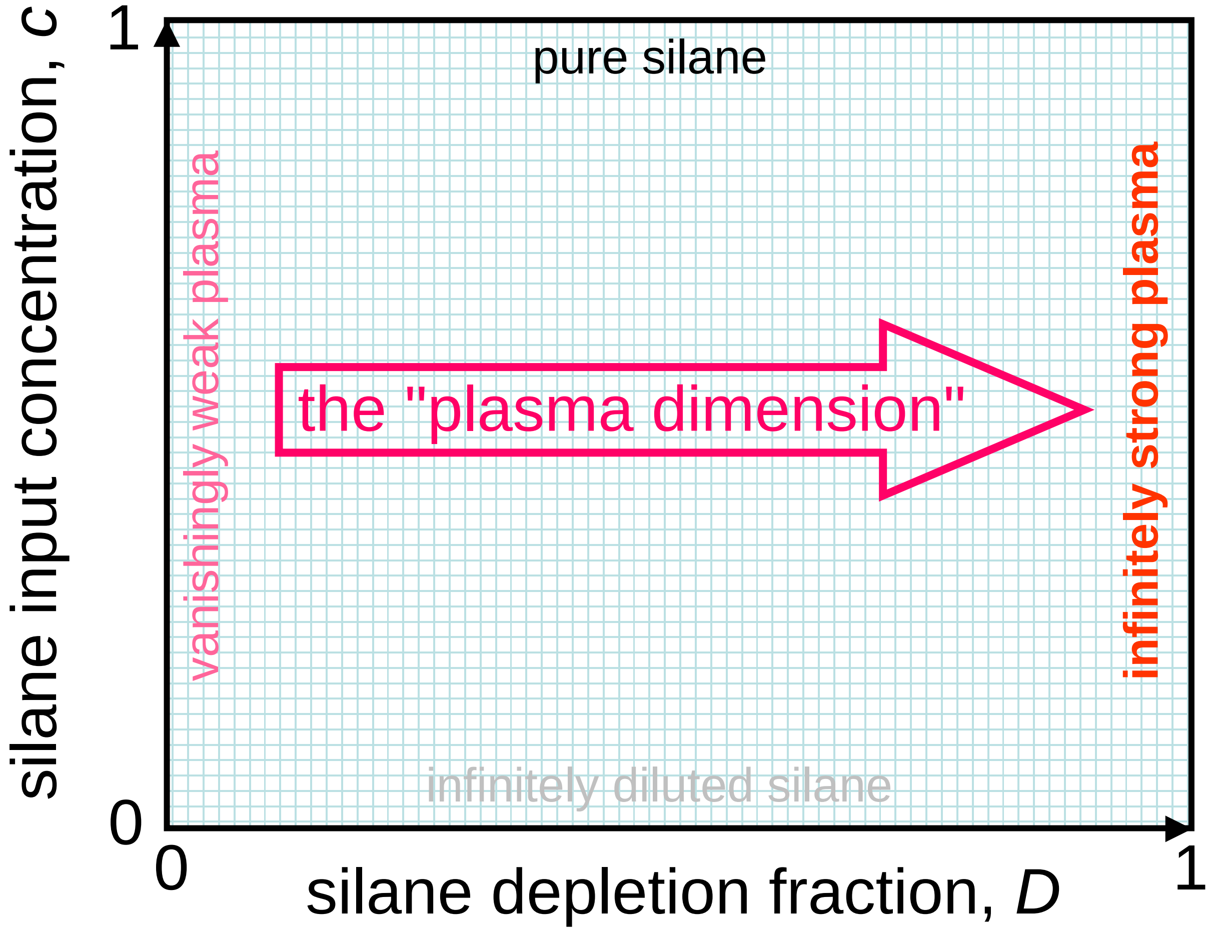
p

Therefore

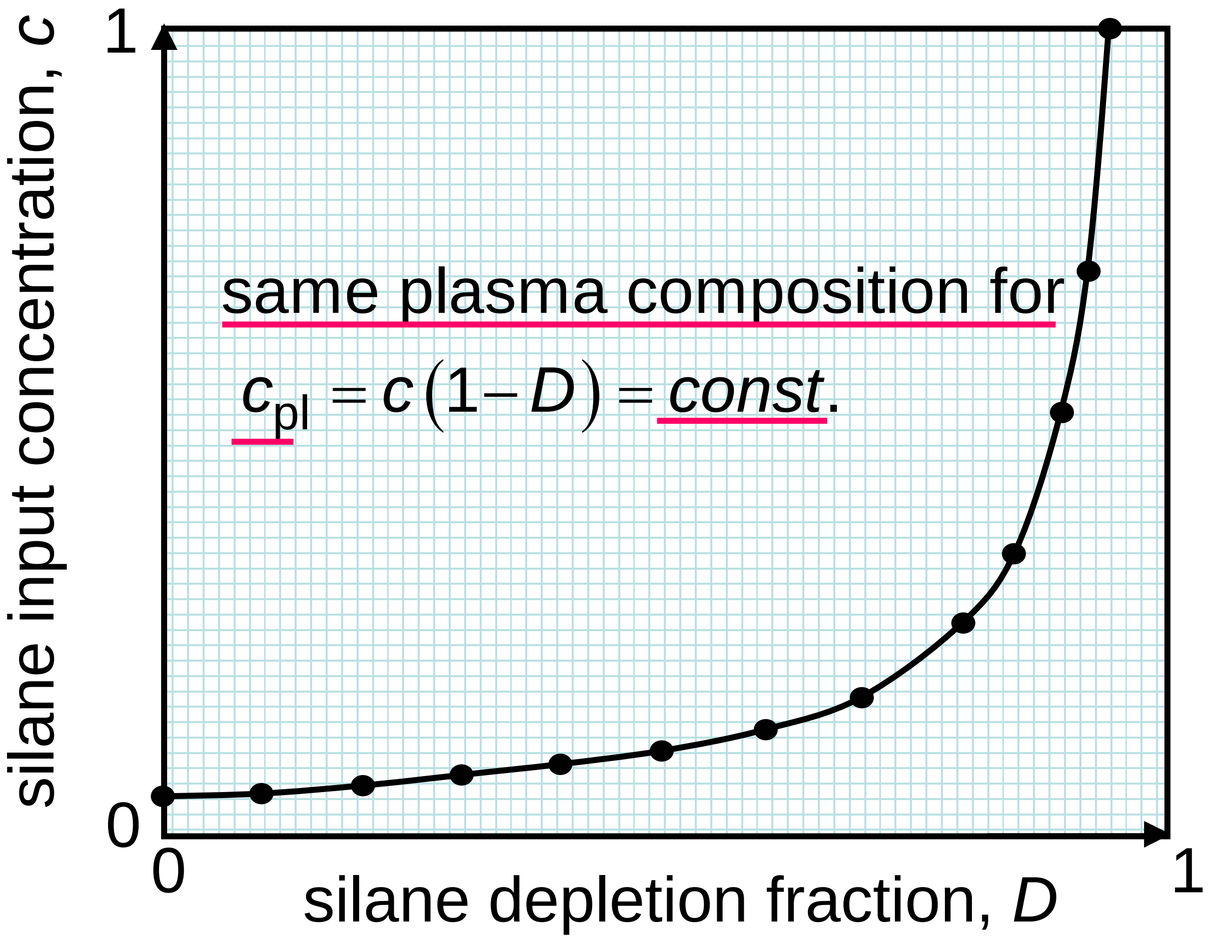
silane concentration in plasma, $c_{pl} = c(1-D)$

2 parameters, c & D, define the plasma composition

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



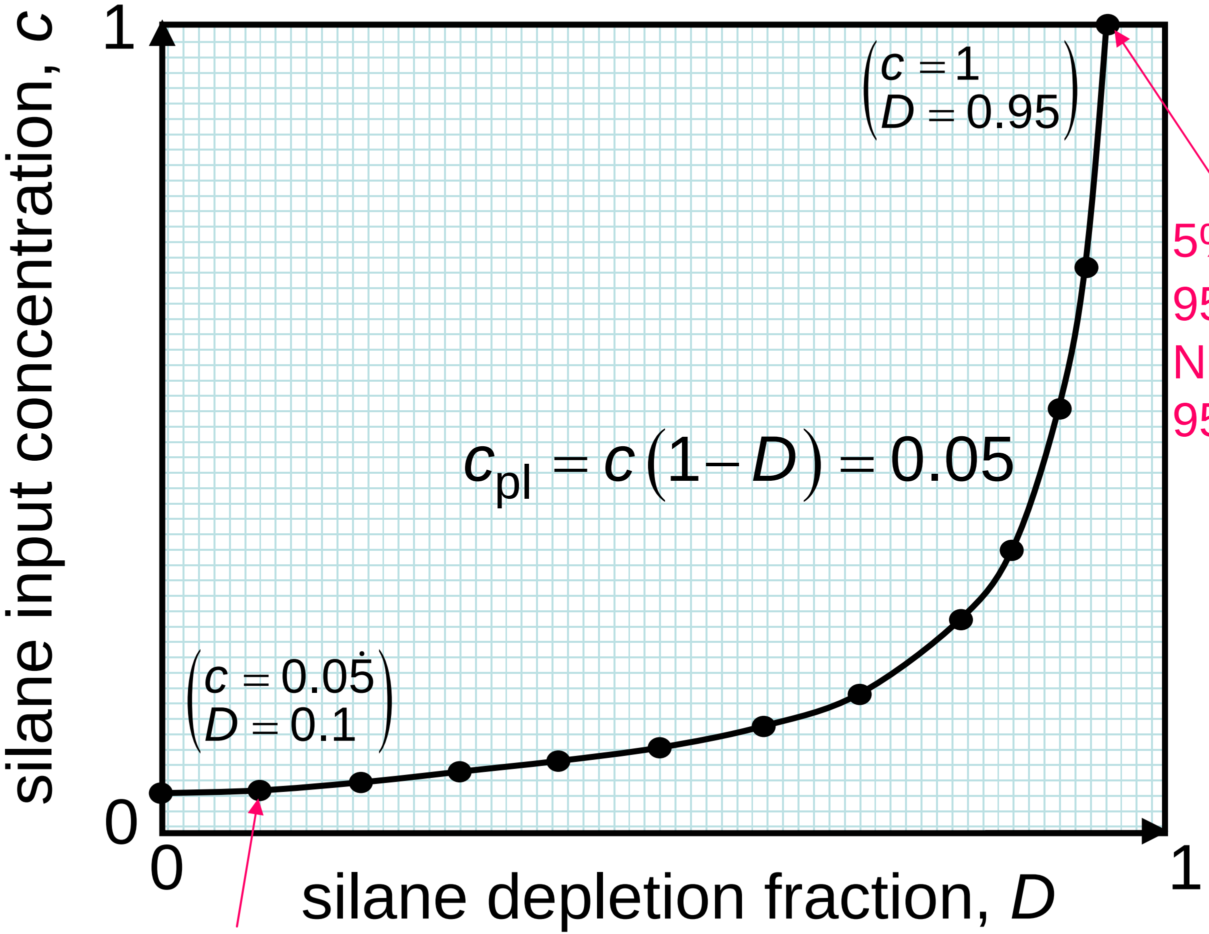
1) Contours of constant plasma composition



same plasma composition for

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

1) Contours of constant plasma composition



$$\begin{pmatrix} c = 1 \\ D = 0.95 \end{pmatrix}$$

$$c_{pl} = c\left(1 - D\right) = 0.05$$

$$\begin{pmatrix} c = 0.0\dot{5} \\ D = 0.1 \end{pmatrix}$$

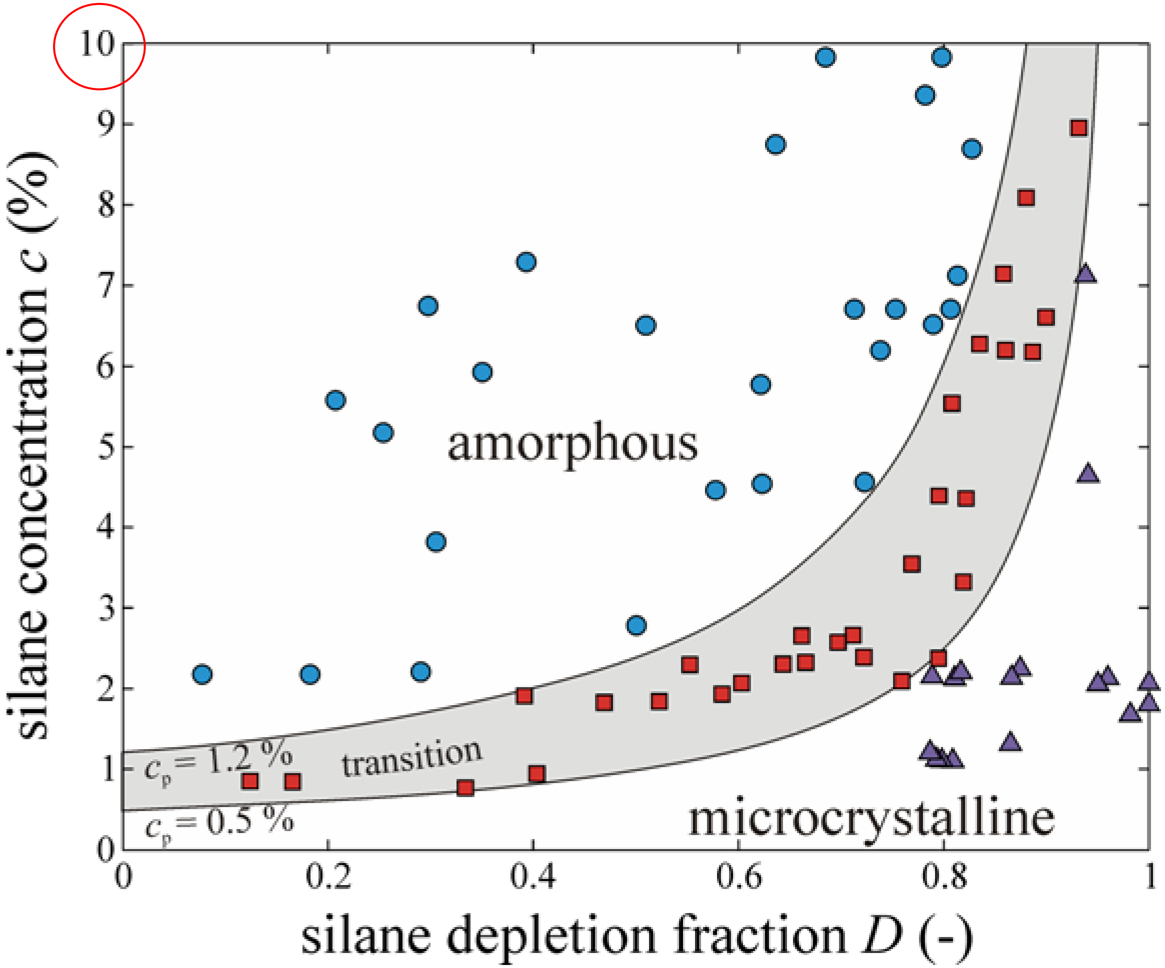
5% silane
95% hydrogen
NO input dilution,
95% depletion

IN THE PLASMA

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

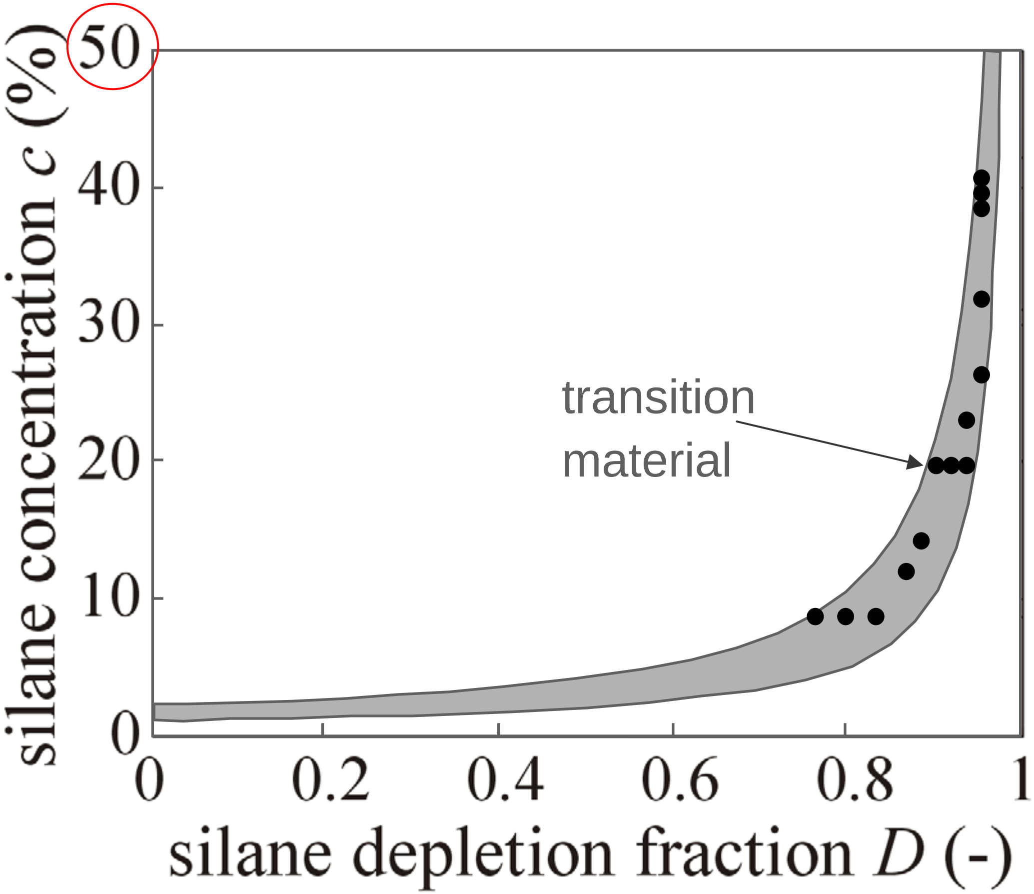
IN THE PLASMA

1) Same plasma composition = same film properties

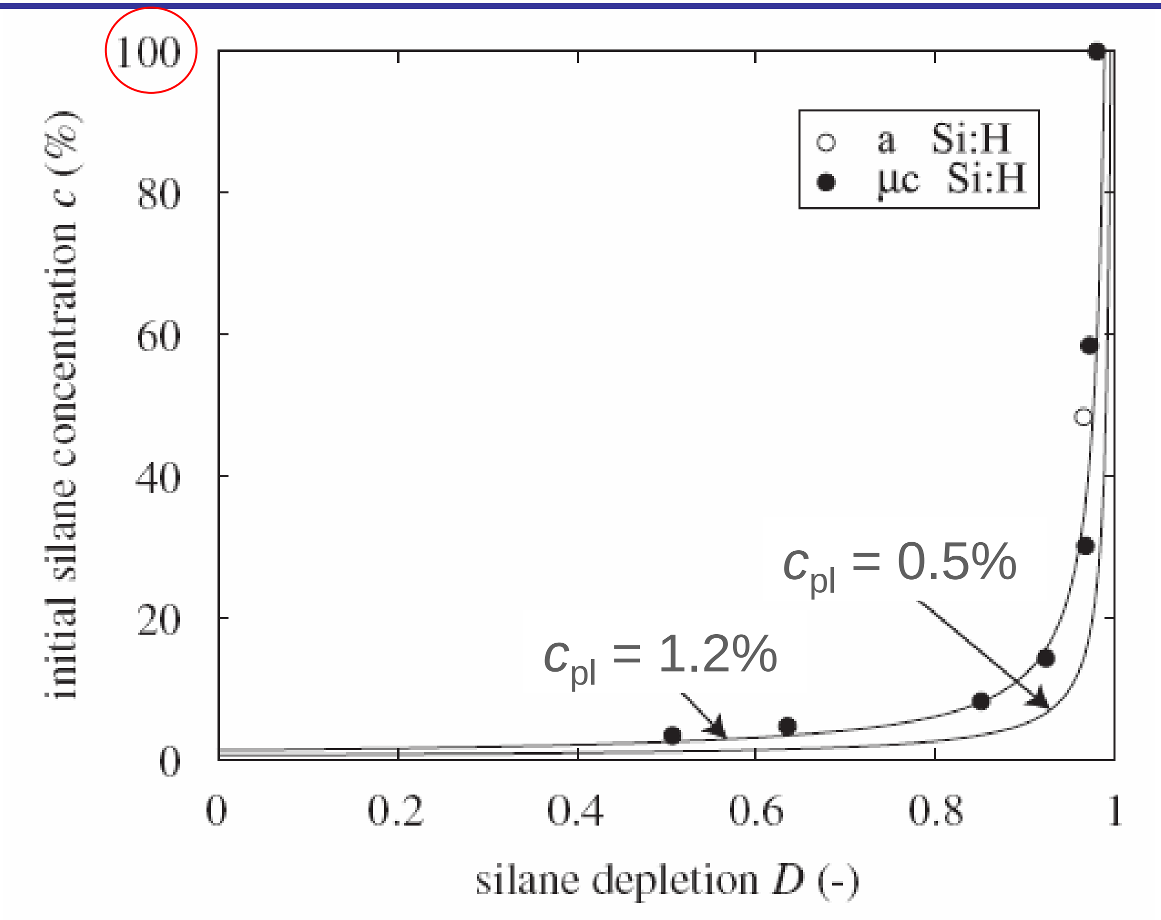


Constant plasma composition, c_{pl}, gives constant film properties

1) Same plasma composition = same film properties

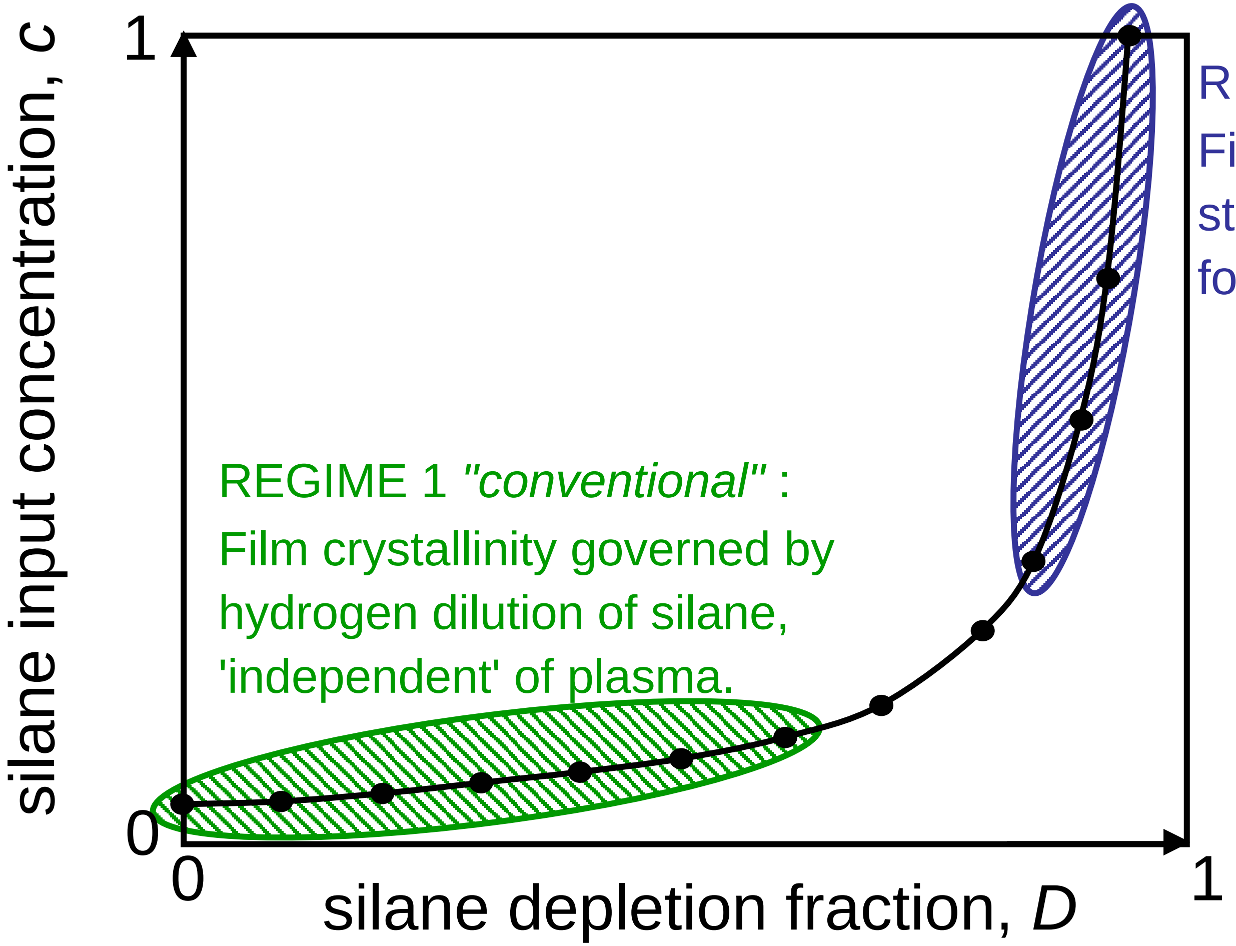


1) Same plasma composition = same film properties



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.

1) Two regimes of operation



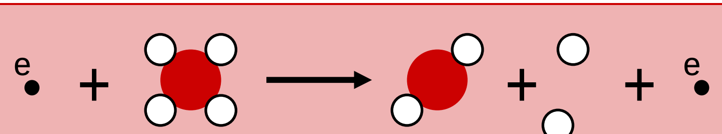
REGIME 1 *"conventional"* :
Film crystallinity governed by
hydrogen dilution of silane,
'independent' of plasma.

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

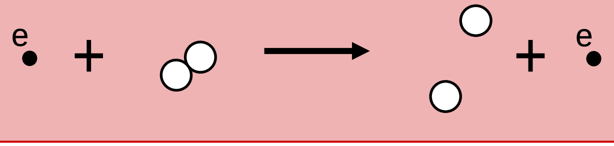
1) Simple plasma chemistry model

Based on a reduced set of gas phase reactions…

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

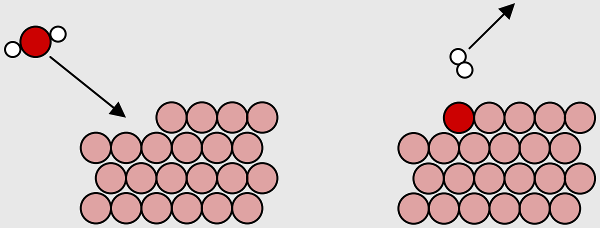


$$e + H_2 \xrightarrow{k_H} 2H + e$$



…and simplified surface reactions.

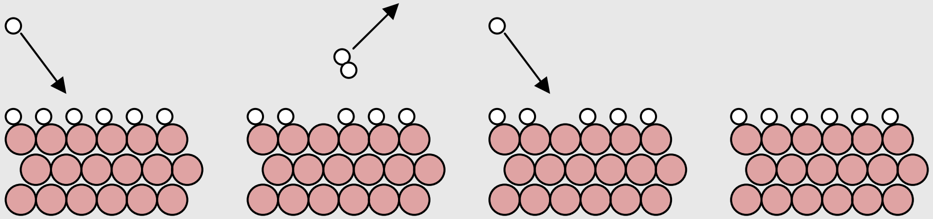
$$SiH_2 \xrightarrow{S} Si_{surf} + H_2$$



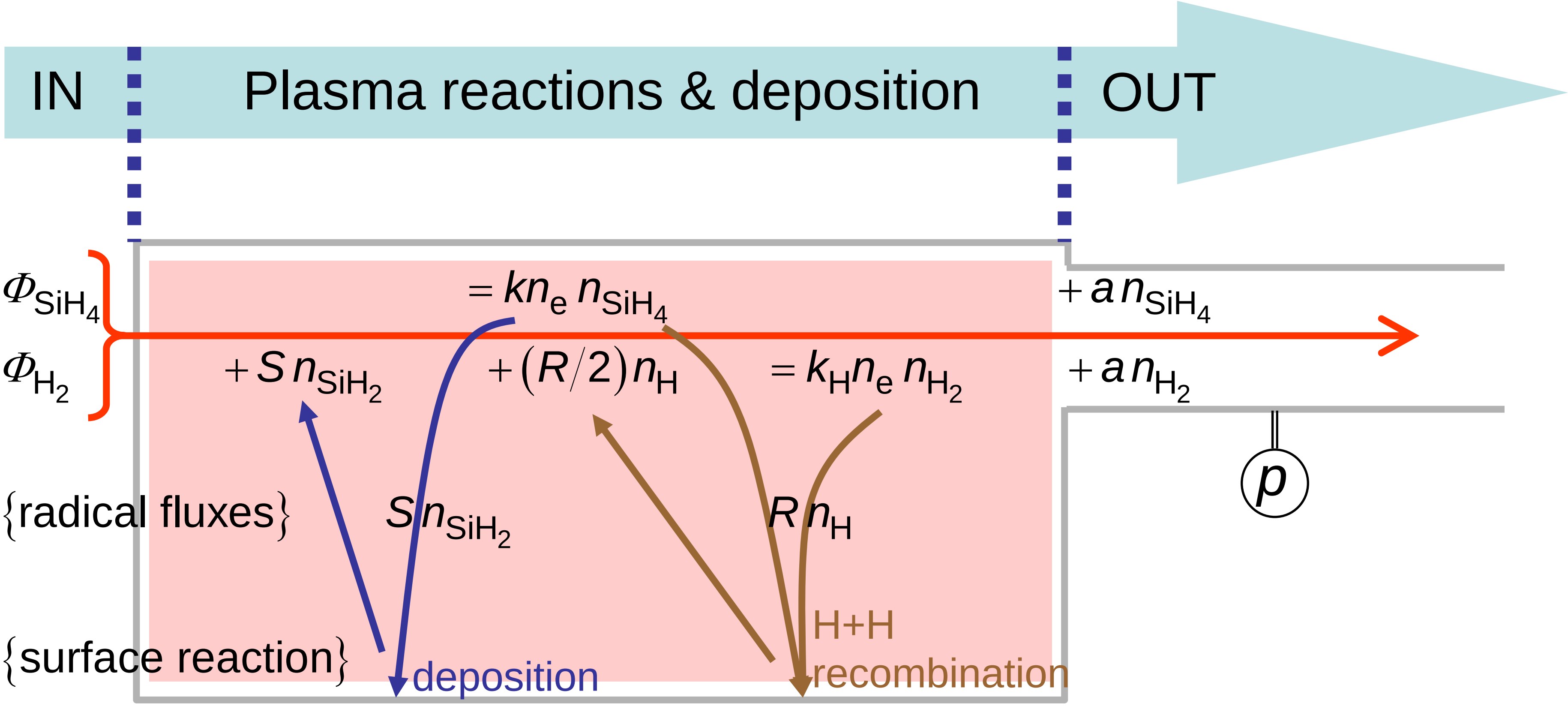
$$H + H_{surf} \longrightarrow H_2 + \text{vacancy}$$

$$H + \text{vacancy} \longrightarrow H_{surf} \quad +$$

$$H \xrightarrow{R} \frac{1}{2} H_2$$



1) Simple, analytical plasma chemistry model



IN

Plasma reactions & deposition

OUT

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

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

{radical fluxes} $S \, n_{SiH_2}$ $R \, n_H$

{surface reaction} deposition H+H recombination

p

- A zero-dimensional model *is* appropriate to showerhead reactors

1) 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.

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

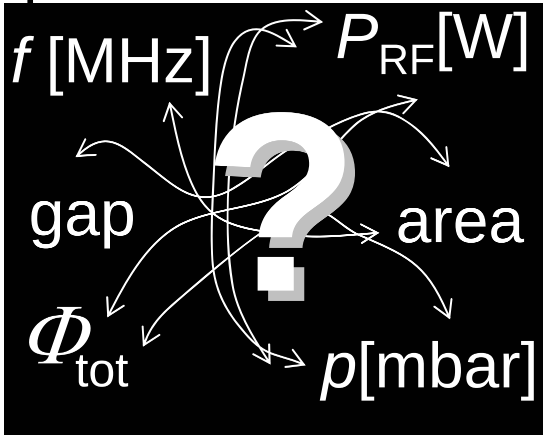
Hydrogen and silane are the dominant partial pressures;

so we can expect radical densities to depend on them.

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

1) Depletion accounts for all of the plasma parameters

plasma black box



analytical model

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

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

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

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

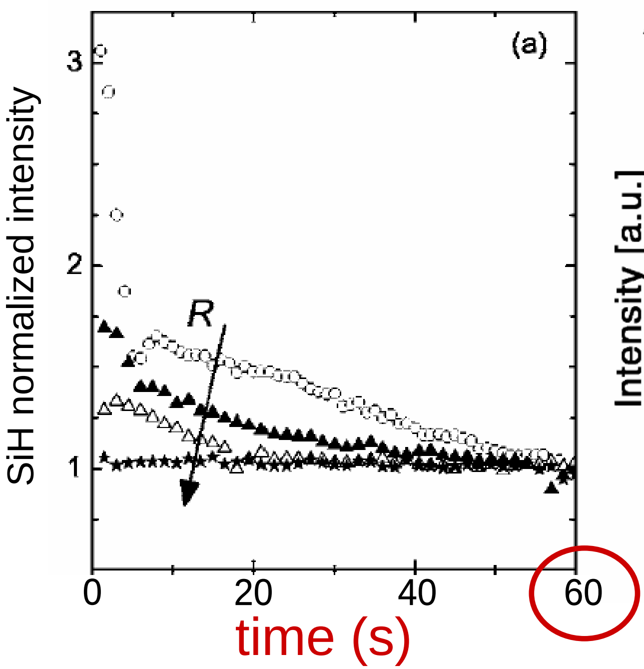
$D\uparrow$ if any of $\{p,\ \mathrm{gap},\ \mathrm{area},\ c,\ P_{RF},\ f\}\uparrow$ &/or $\{\Phi_{total},\ T_{gas}\}\downarrow$

✓ 1) The "plasma dimension" for plasma deposition of μc-Si:H

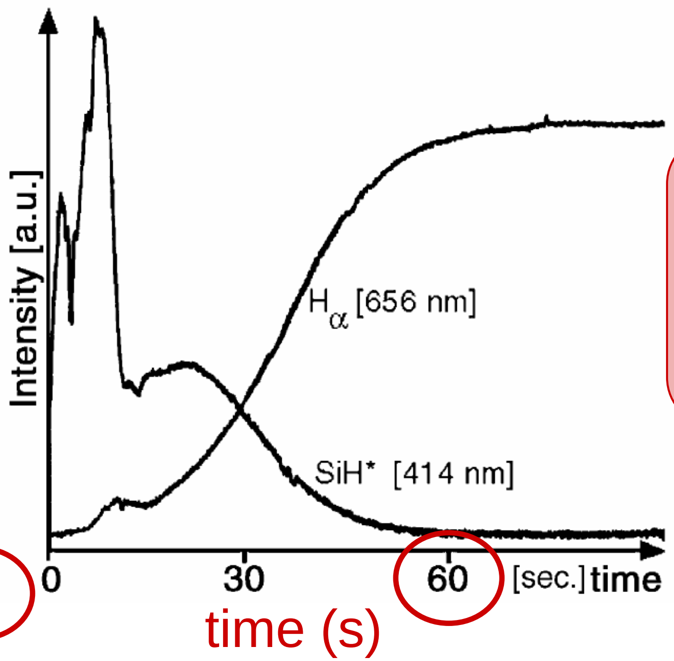
2) Direct pumping of a plasma reactor

2) Plasma chemistry equilibration time to steady-state depletion

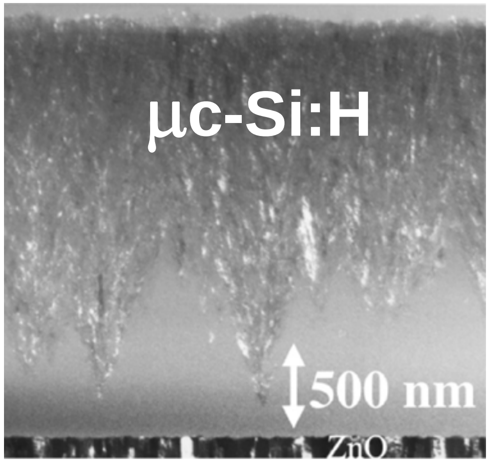
van den Donker *et al* (2005)



Feitknecht *et al* (2002)



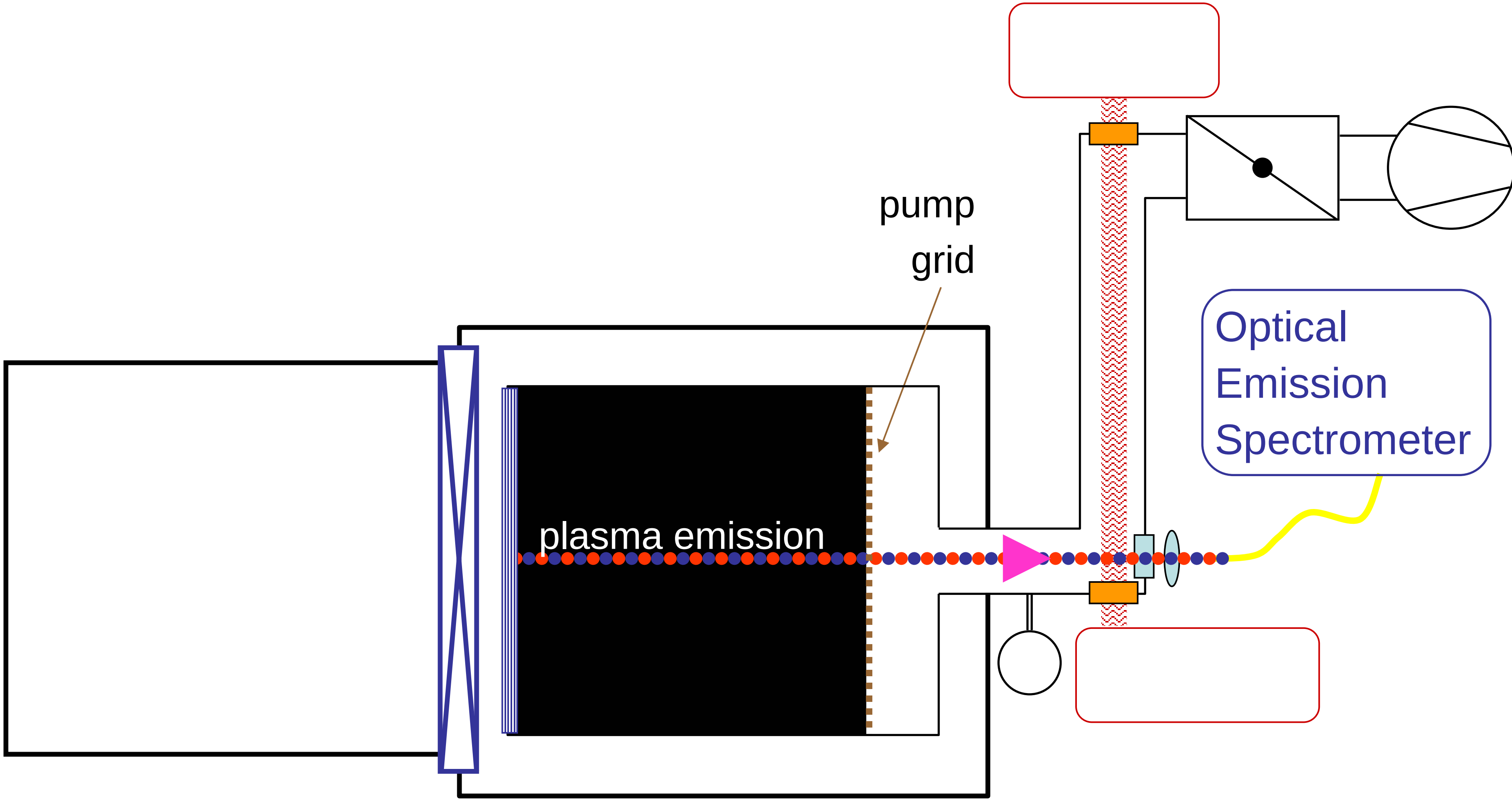
Almost a minute to reach the plasma composition suitable to grow μc-Si:H...



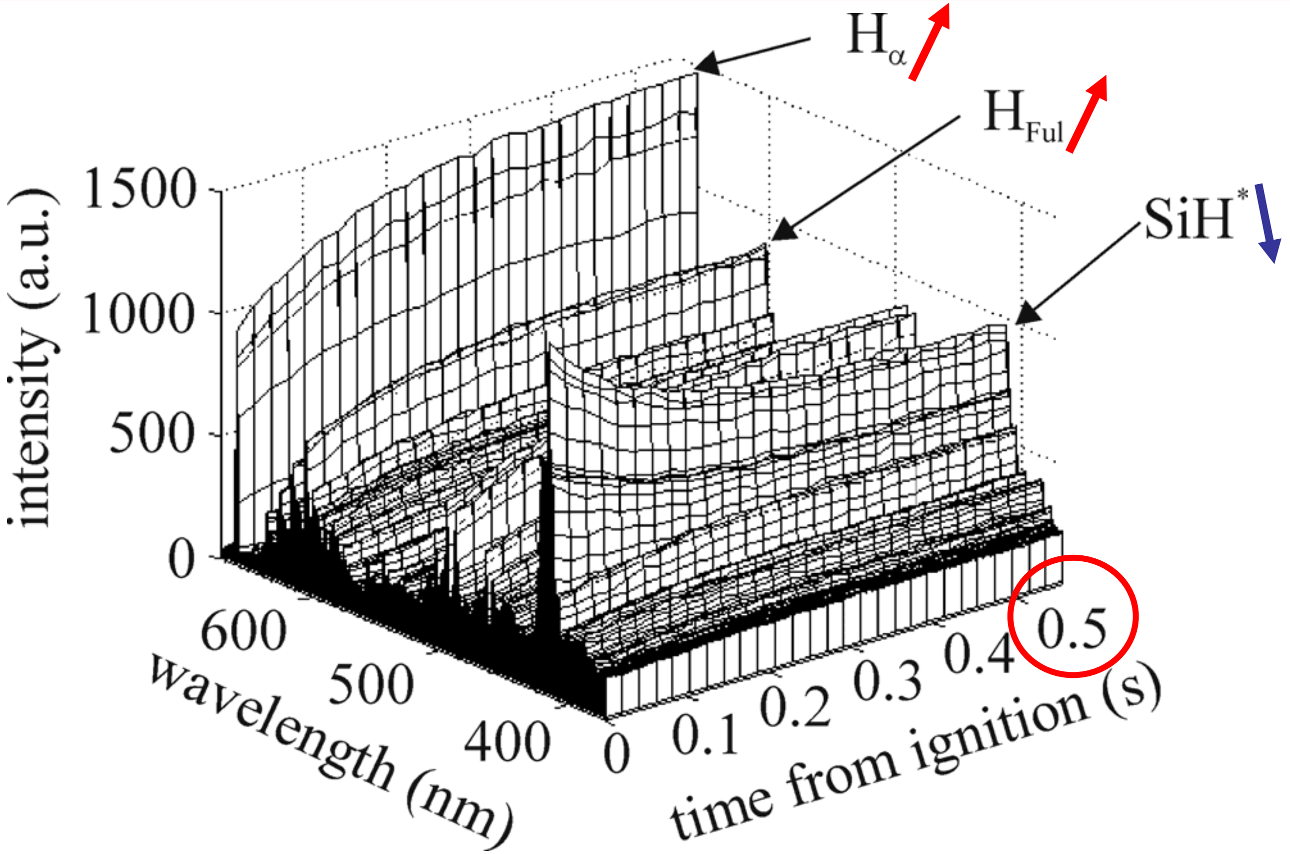
... thick amorphous incubation layer

... deteriorates solar cell performance.

2) OES: Non-intrusive, rapid diagnostic for equilibration time



2) Time-resolved optical emission spectrum from plasma ignition



Emission from silane radicals, SiH*, <u>falls</u> as the silane becomes depleted

Emission from excited molecular and atomic hydrogen <u>rises</u> as its partial pressure rises

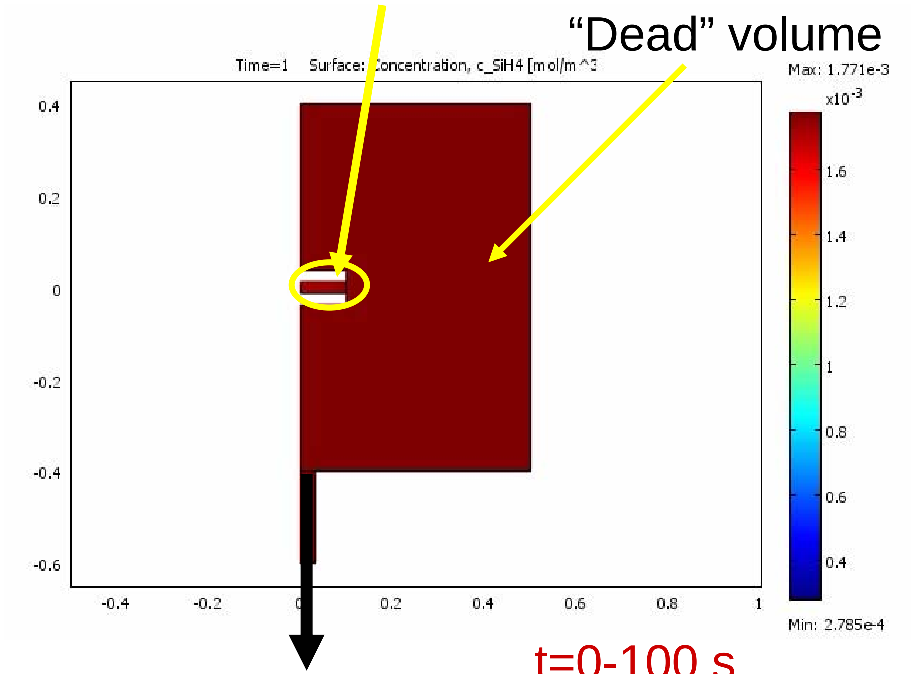
<u>The plasma chemistry equilibration time is less than one second!</u>

2) Compare open and closed reactors (numerical)

Open laboratory reactor
(axial symmetry)

Closed, directly-pumped plasma box
(lateral view)

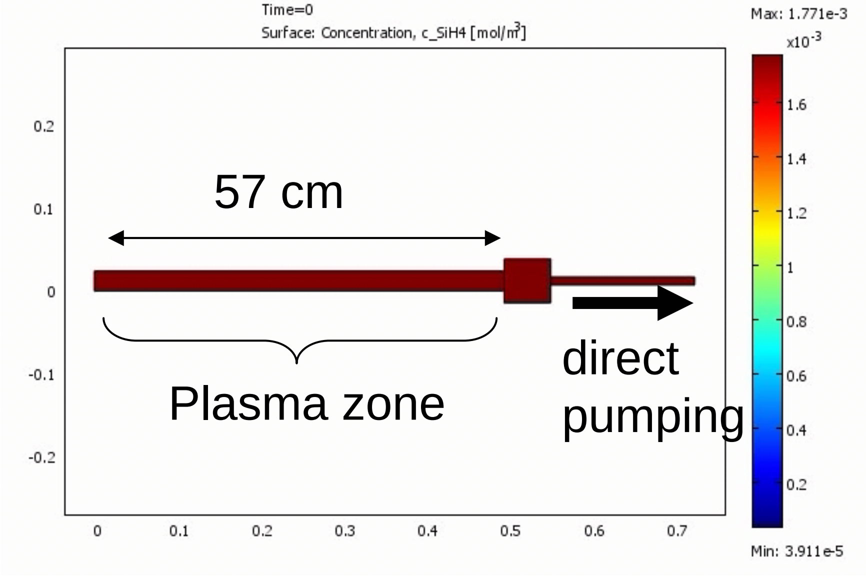
Plasma zone (20 cm in diameter)



“Dead” volume

indirect pumping

t=0-100 s



57 cm

Plasma zone

direct pumping

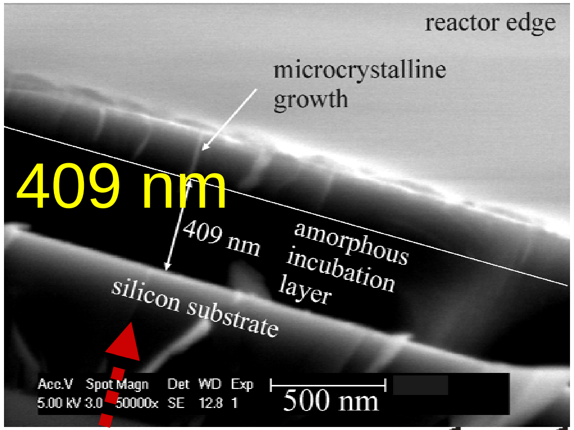
t=0-1 s

time to steady-state > 100 s !

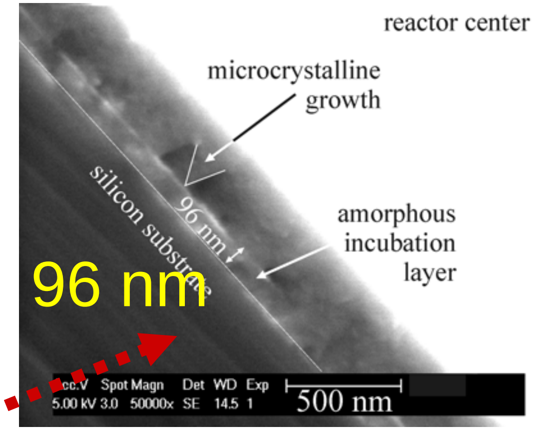
time to steady-state < 1 s !

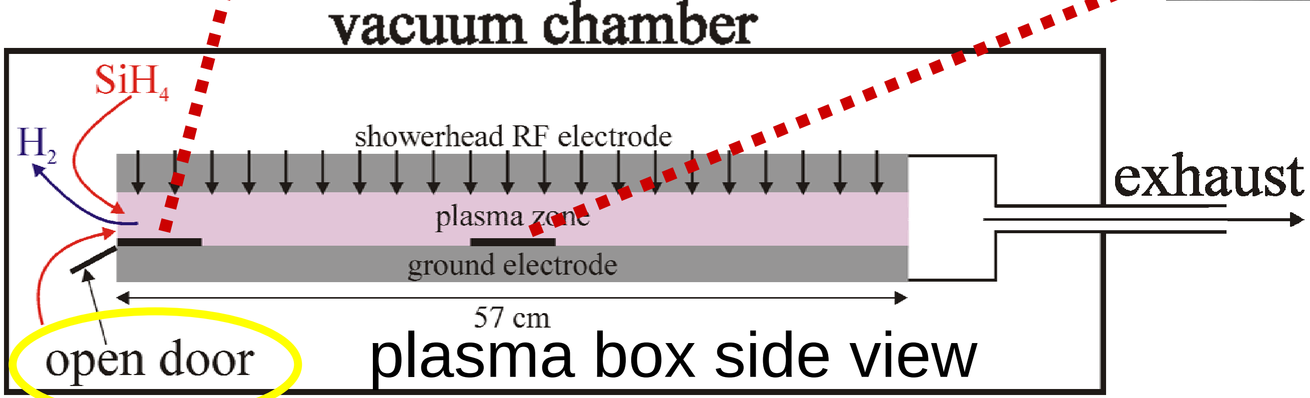
Silane back-diffusion from any intermediate dead volume increases the equilibration time.

2) Practical consequence of the pumping configuration

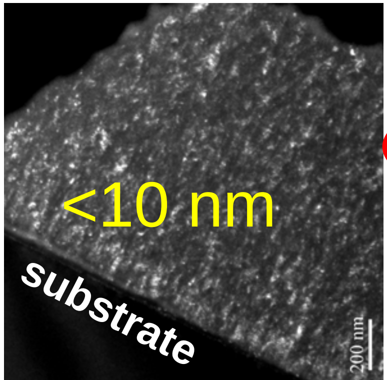


Amorphous incubation layers with *open* door





plasma box side view



But the door is normally *closed*, the amorphous incubation layer is then thinner than 10 nm.

CRPP

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Two Conclusions

1. 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.

- monitored non-intrusively by FTIR in the pumping line.

2. Rapid equilibration of plasma chemistry requires a closed, directly-pumped showerhead reactor with a uniform plasma - avoid gas circulation between the plasma and any dead volumes.

- monitored non-intrusively by OES in the pumping line.

Refs. B. Strahm *et al*, Plasma Sources, Sci. Technol. **16** 80 (2007).

A. A. Howling *et al*, Plasma Sources, Sci. Technol. **16** 679 (2007).

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