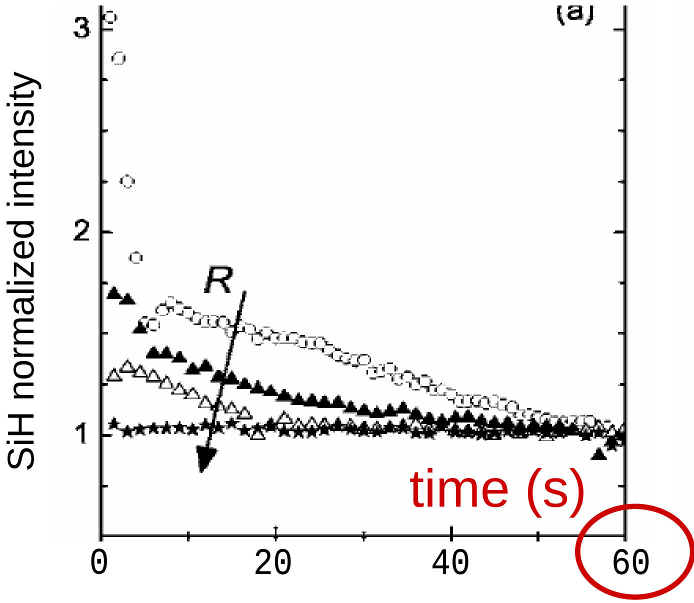
IV. Uniformity in time: rapid equilibration to steady-state process parameters. Direct pumping.

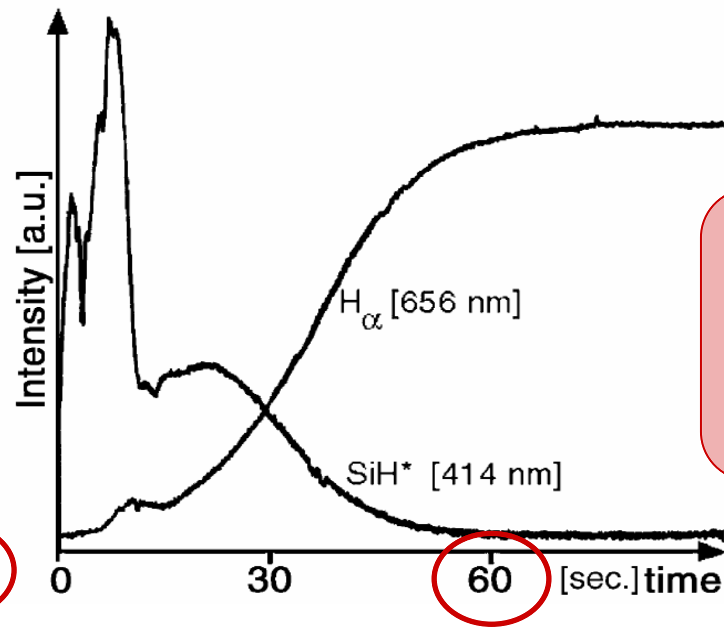
V. So where is the problem? - Causes of non-uniformity. Some recommendations.

Plasma chemistry equilibration time to steady-state depletion

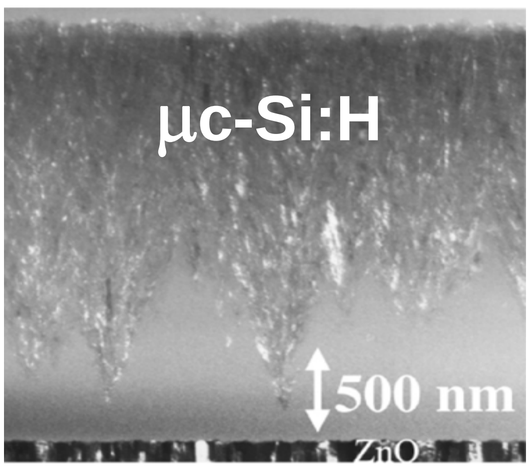
M. N. van den Donker, B. Rech, F. Finger, W. M. M. Kessels, and M. C. M. van de Sanden, *Appl. Phys. Lett.* **87**, 263503 (2005)



L. Feitknecht, J. Meier, P. Torres, J. Zuercher, and A. Shah, *Sol. Energy Mater. Sol. Cells* **74**, 539 (2002)



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

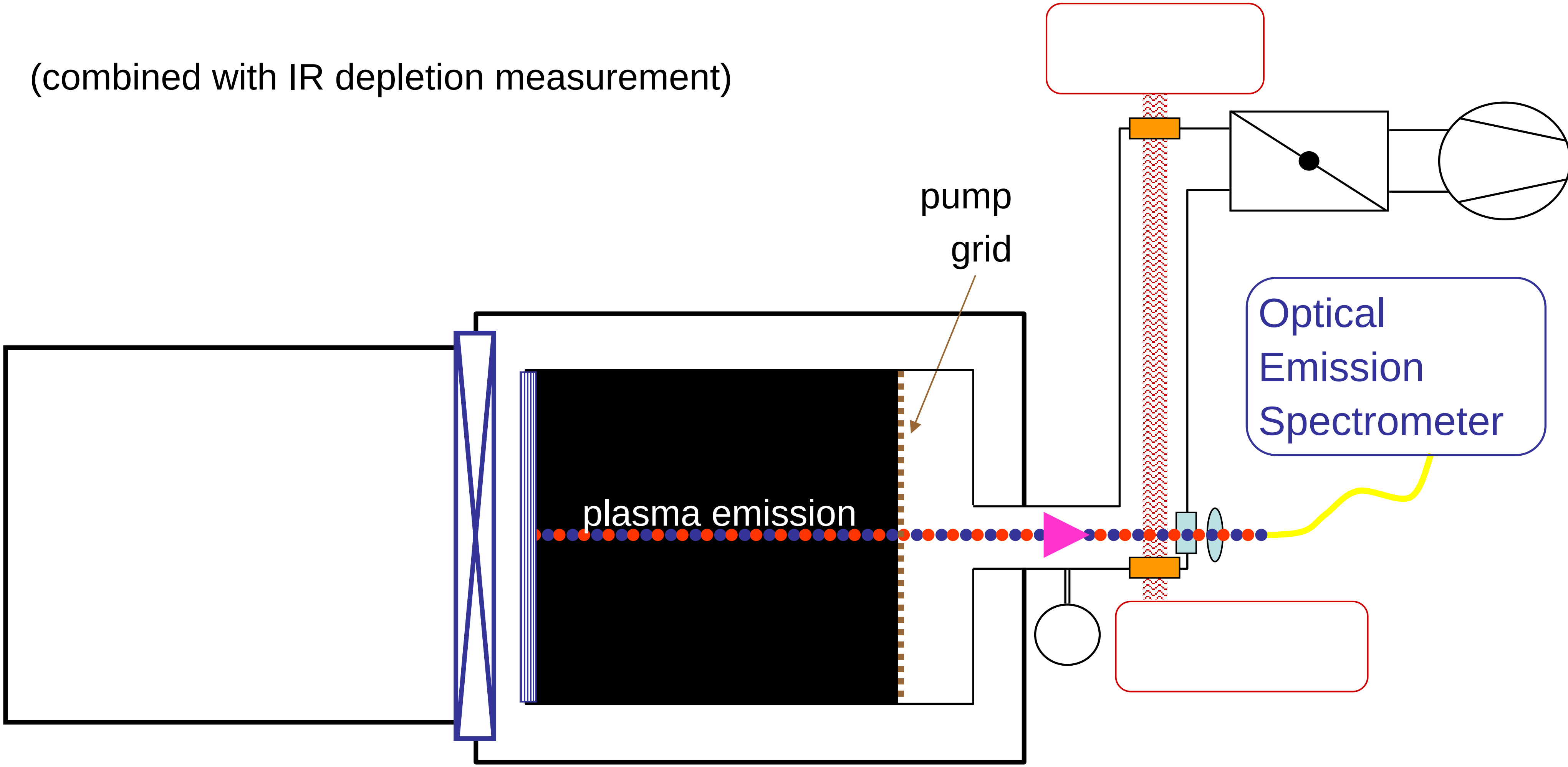


... thick amorphous incubation layer

... deteriorates solar cell performance.

OES: Non-intrusive, rapid diagnostic for equilibration time

(combined with IR depletion measurement)



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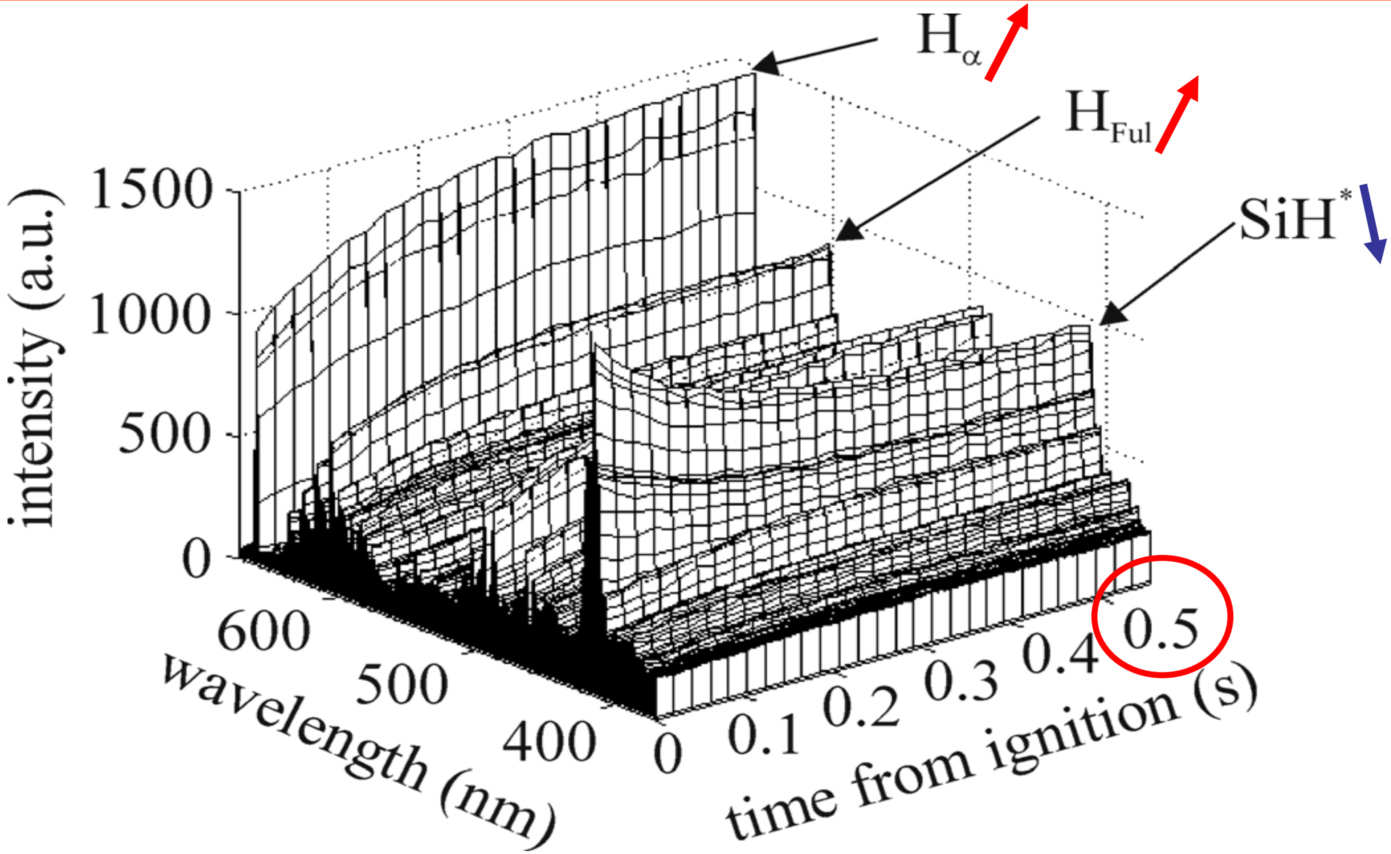
EPFL ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Time-resolved optical emission spectrum from plasma ignition



Emission from silane radicals, SiH*, falls as the silane becomes depleted

Emission from excited molecular and atomic hydrogen rises as its partial pressure rises

The plasma chemistry equilibration time is much less than one second!

A. A. Howling, B. Strahm, P. Colsters, L. Sansonnens, and Ch. Hollenstein, *Plasma Sources, Sci. Technol.* **16,** 679 (2007).

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The gas residence time...

The gas residence time, $\tau_{\mathrm{res}} = 1/a_0$, is the time to replace all the gas in the reactor by flow in and pumping out:

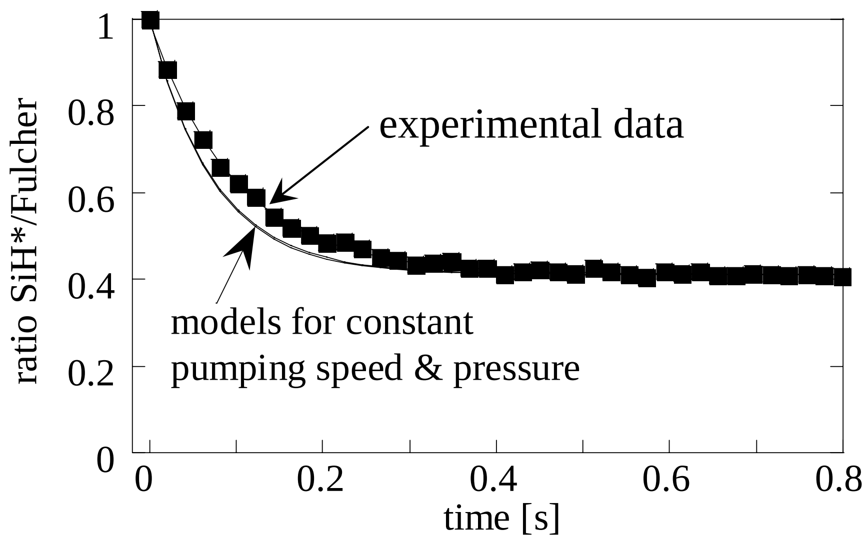
The inverse gas residence time (no plasma), $a_0\left[\mathrm{s}^{-1}\right] = \dfrac{\Phi\left[\mathrm{molecules}\cdot\mathrm{m}^{-3}\cdot\mathrm{s}^{-1}\right]}{n_{\mathrm{tot}}\left[\mathrm{molecules}\cdot\mathrm{m}^{-3}\right]} = 6.1\times10^{-6}\,\dfrac{T_{\mathrm{gas}}\left[\mathrm{K}\right]F_{\mathrm{tot}}\left[\mathrm{sccm}\right]}{p\left[\mathrm{Pa}\right]V_{\mathrm{box}}\left[\mathrm{m}^{3}\right]}$.

For this example, $a_0 = 6.1\times10^{-6}\,\dfrac{500\times500}{40\times0.0067} = 5.7\ \mathrm{s}^{-1}$.

The gas residence time (no plasma), $\tau_{\mathrm{res}} = 1/a_0 = 0.18$ seconds.

... and the plasma chemistry equilibration 1/e time

Use the zero-dimensional, time-dependent analytical model to calculate the 1/e equilibration time :



Assuming constant pumping speed, $a = a_0$,

the reaction rate balance for silane is

$$SiH_4: \quad \Phi_{SiH_4} - (kn_e + a_0)\, n_{SiH_4} = \frac{dn_{SiH_4}}{dt}$$

$$\therefore \quad \frac{n_{SiH_4}(t)}{n_{SiH_4}(0)} = 1 - D\left[1 - \exp\left(-\frac{t}{\tau_{eq}}\right)\right],$$

where the plasma chemistry equilibration 1/e time, $\tau_{eq} = \frac{(1-D)}{a_0} < \tau_{res} = \frac{1}{a_0}.$

For this example, $\tau_{eq} = \frac{(1-0.57)}{5.7} = 0.076$ s. good agreement with experiment

- the zero-dimensional model was used to predict the required time resolution (~ 20 ms) of the optical emission spectrometer for this experiment.

(for constant pressure calculations, see A. A. Howling, B. Strahm, P. Colsters, L. Sansonnens, and Ch. Hollenstein, *Plasma Sources, Sci. Technol.* **16,** 679 (2007))

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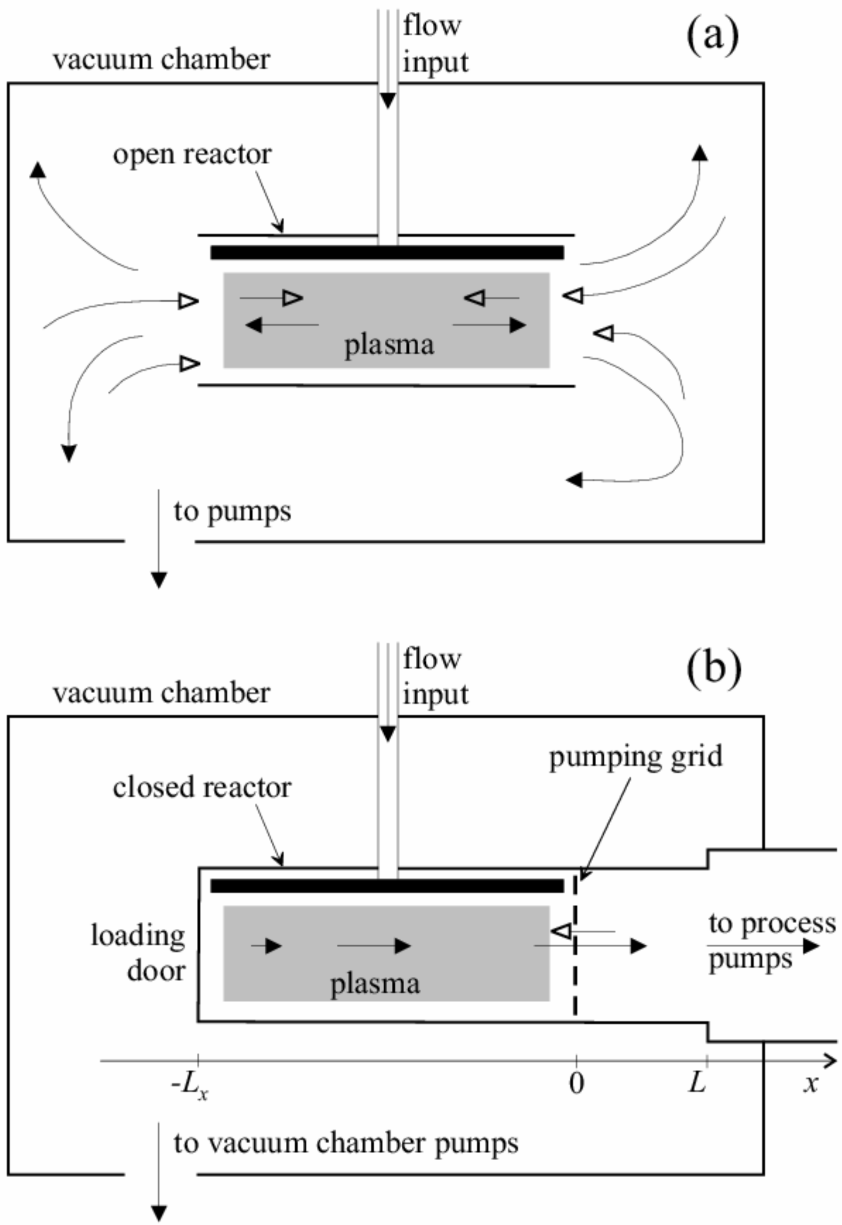
Compare open and closed reactors (descriptive)

Black arrows: convective flow

White arrows: diffusive flow (disappear in steady state)



- showerhead reactor
- open electrodes
- indirect pumping at the wall

Don't design the reactor around your exotic diagnostic technique; design the reactor for the process!

- showerhead reactor
- closed electrodes
- directly pumped plasma reactor
- differential pumping of vacuum chamber

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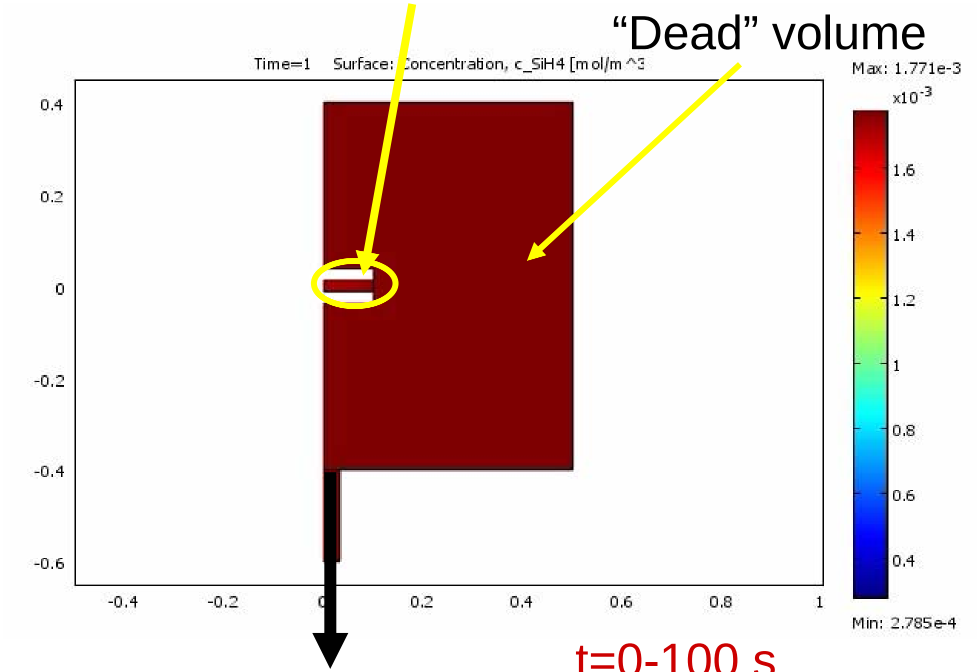
Compare open and closed reactors (numerical)

Open laboratory reactor
(axial symmetry)

Plasma zone (20 cm in diameter)

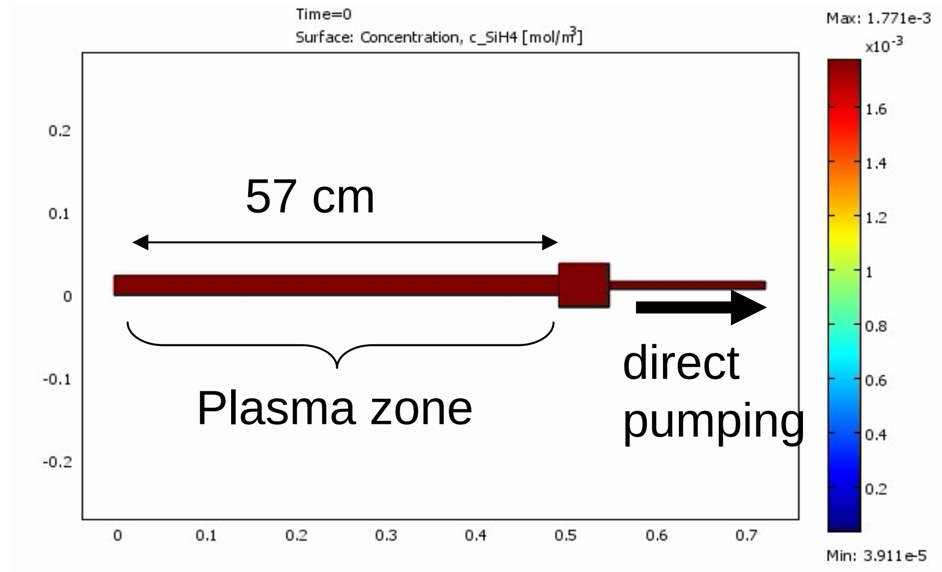


indirect pumping

t=0-100 s

time to steady-state > 100 s !

Closed, directly-pumped plasma box
(lateral view)



t=0-1 s

time to steady-state < 1 s !

Silane back-diffusion from any dead volume between the reactor and the pumps increases the equilibration time.

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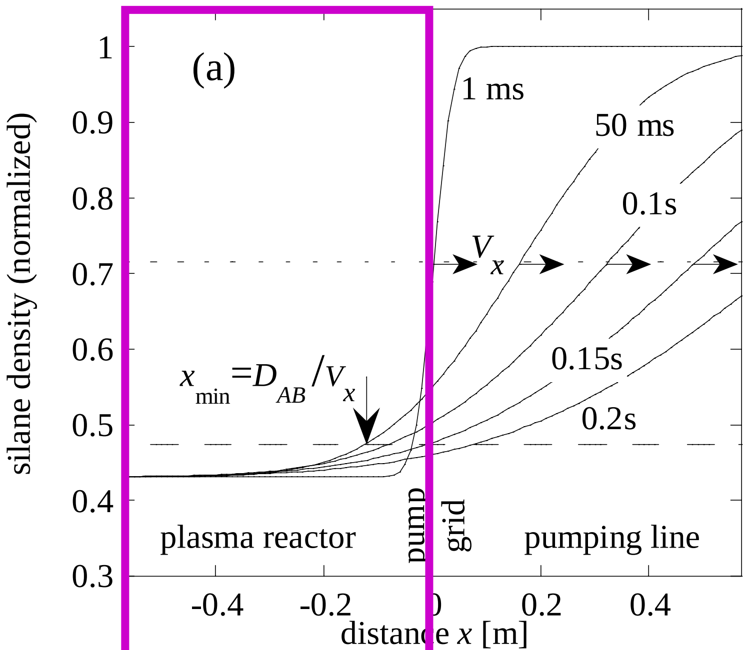
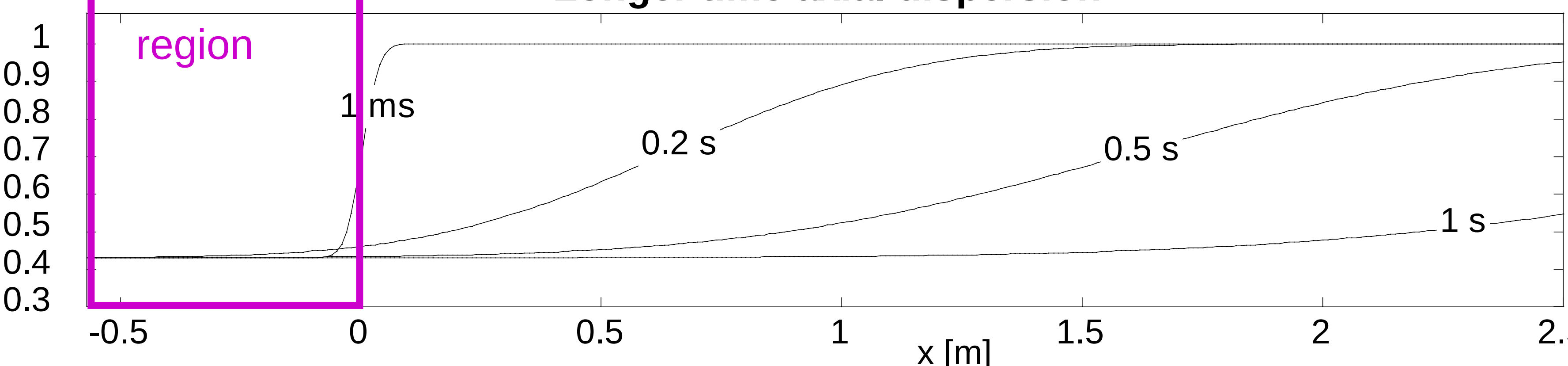
Dispersive axial flow model (analytic)

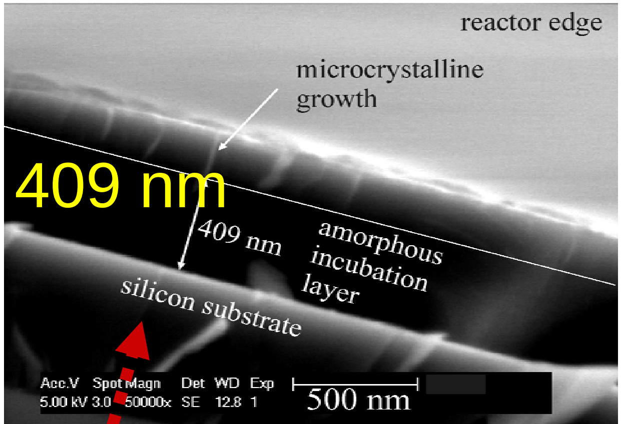


- An advantage of direct pumping is that the concentration gradient is convected downstream away from the plasma.
- Retro-diffusion is strongly reduced.
- Equilibration time is the minimum theoretically possible.

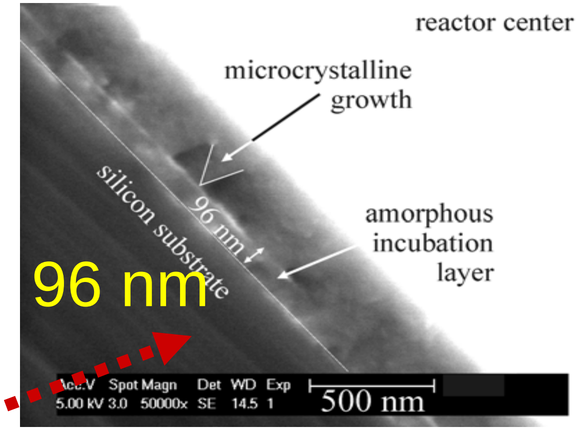
Longer time axial dispersion

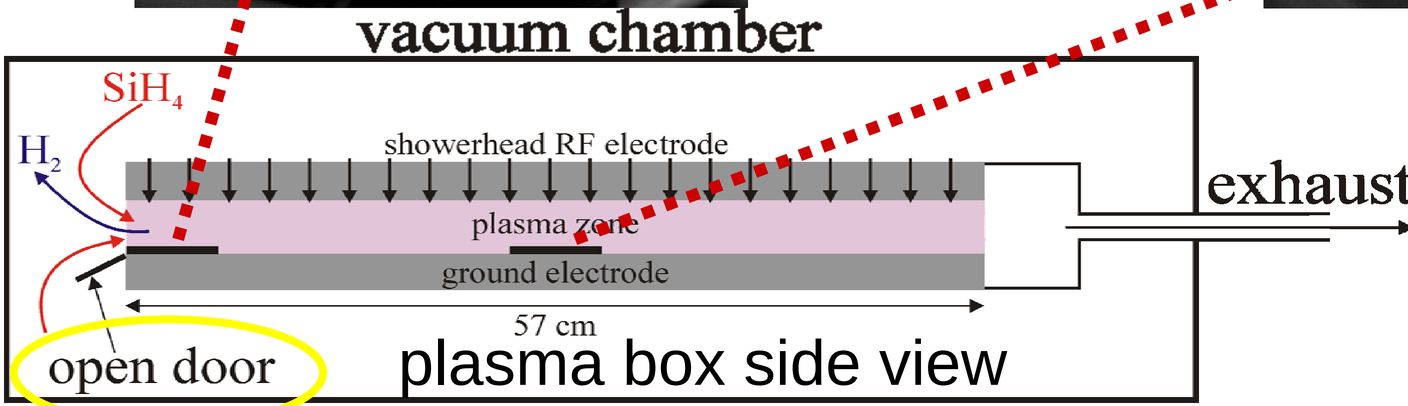


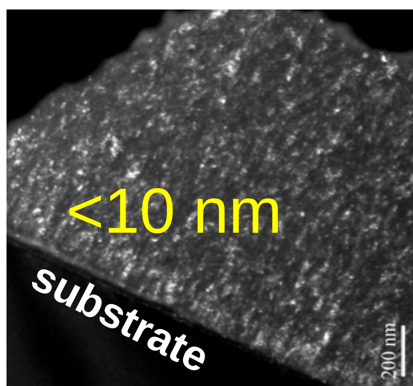
Practical consequence of the pumping configuration



Amorphous incubation layers with *open* door







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

Intermediate Conclusions

For plasma conditions uniform in *time*:

- 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 optical emission spectroscopy via the pumping grid.

Ref. A. A. Howling, B. Strahm, P. Colsters, L. Sansonnens and Ch. Hollenstein,
Plasma Sources, Sci. Technol. **16,** 679 (2007).