

Growth Species During the Plasma Assisted Deposition of Amorphous, Hydrogenated Carbon Films

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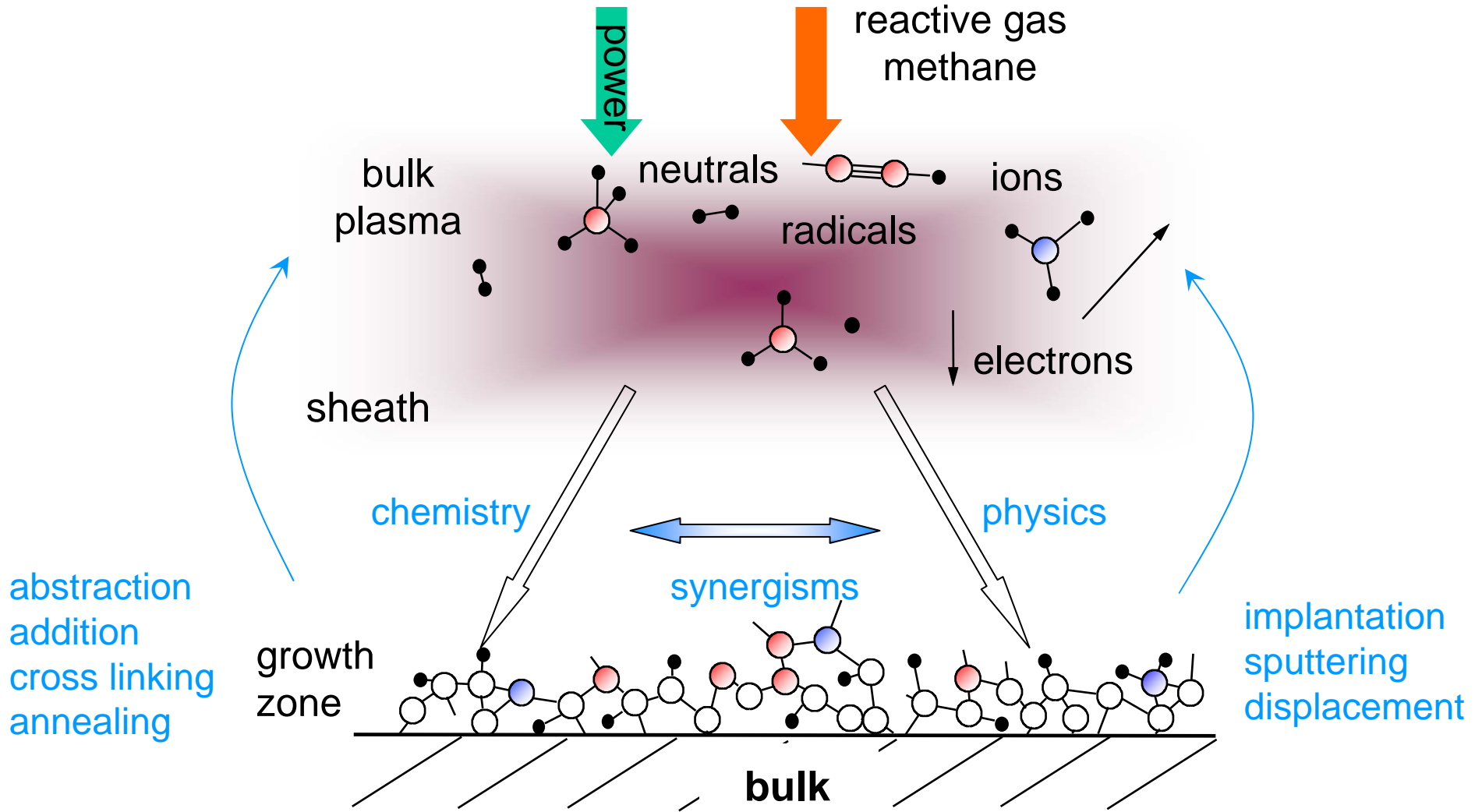
Prof. Achim von Keudell



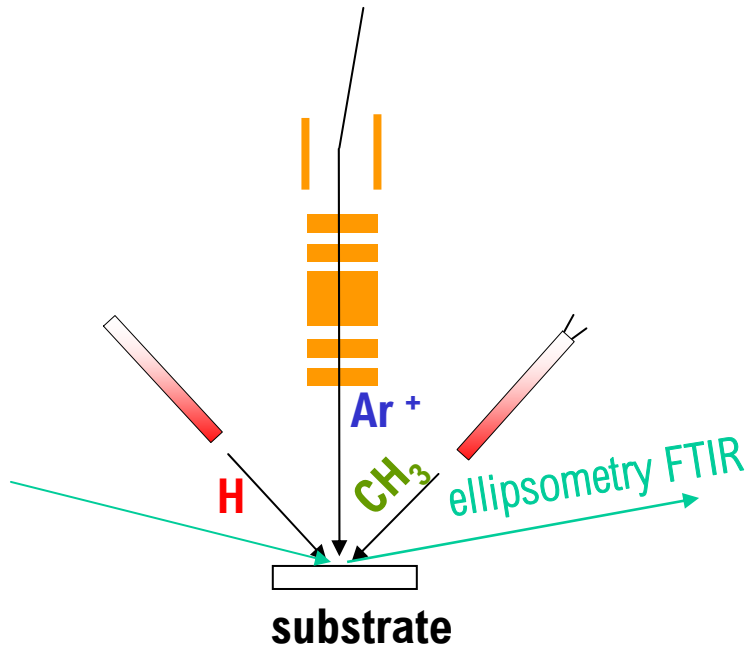
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how do a-C:H film grow?

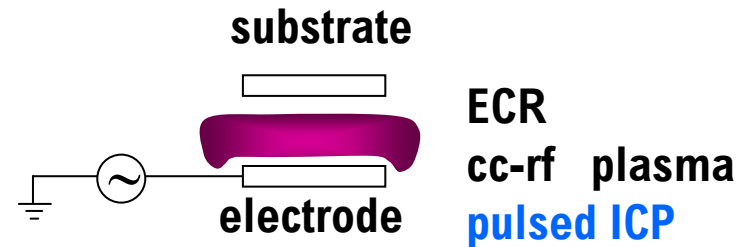


1. quantified beam experiments



- + "easy" interpretation
- + isolation of microscopic mechanism
- "artificial plasma"

2. plasma experiments



diagnostics:

ellipsometry
FTIR
QMS, PM, RFA
cavities...

- + real life
- interpretation ambiguous
- complex particle zoo
- quantification of fluxes?

ambiguous statements in literature about the dominant growth precursor:

CH_3 because most abundant radical

C_2H_y because highly reactive

ions because greatly influence film properties

problem :

correlations in multi-component systems not meaningful

(correlation \neq causality:

see declining number of storks and babies over the last 100 years!)

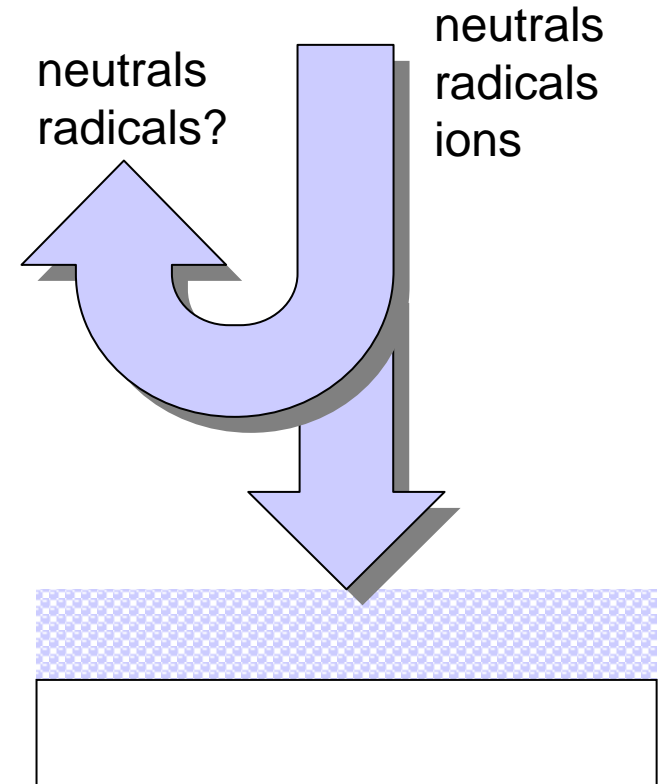
necessity: establishing the carbon balance

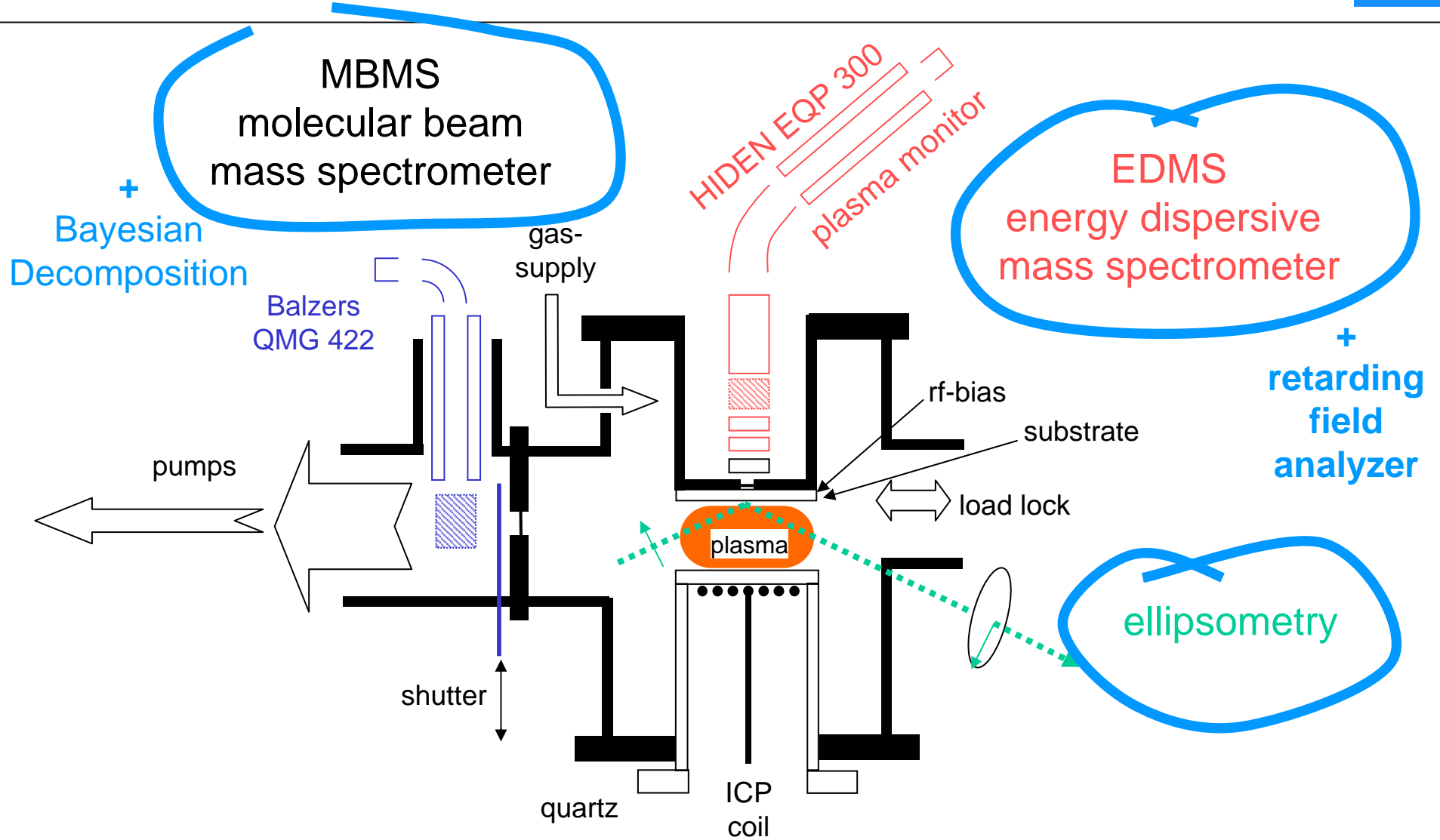
quantitative measurement of net growth flux
(= particle fluxes · sticking)

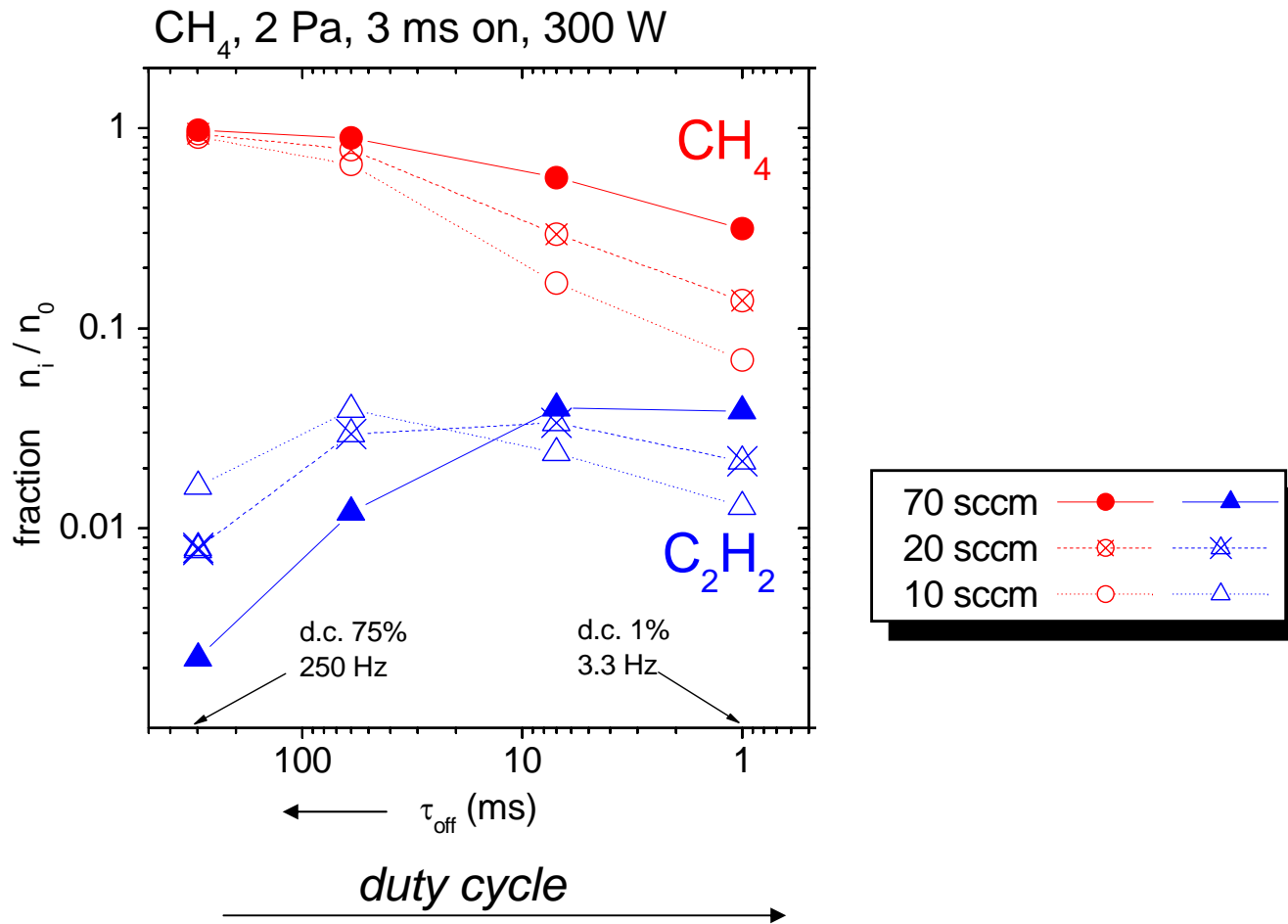
and

total growth rate
(= incorporated carbon atoms / area / time)

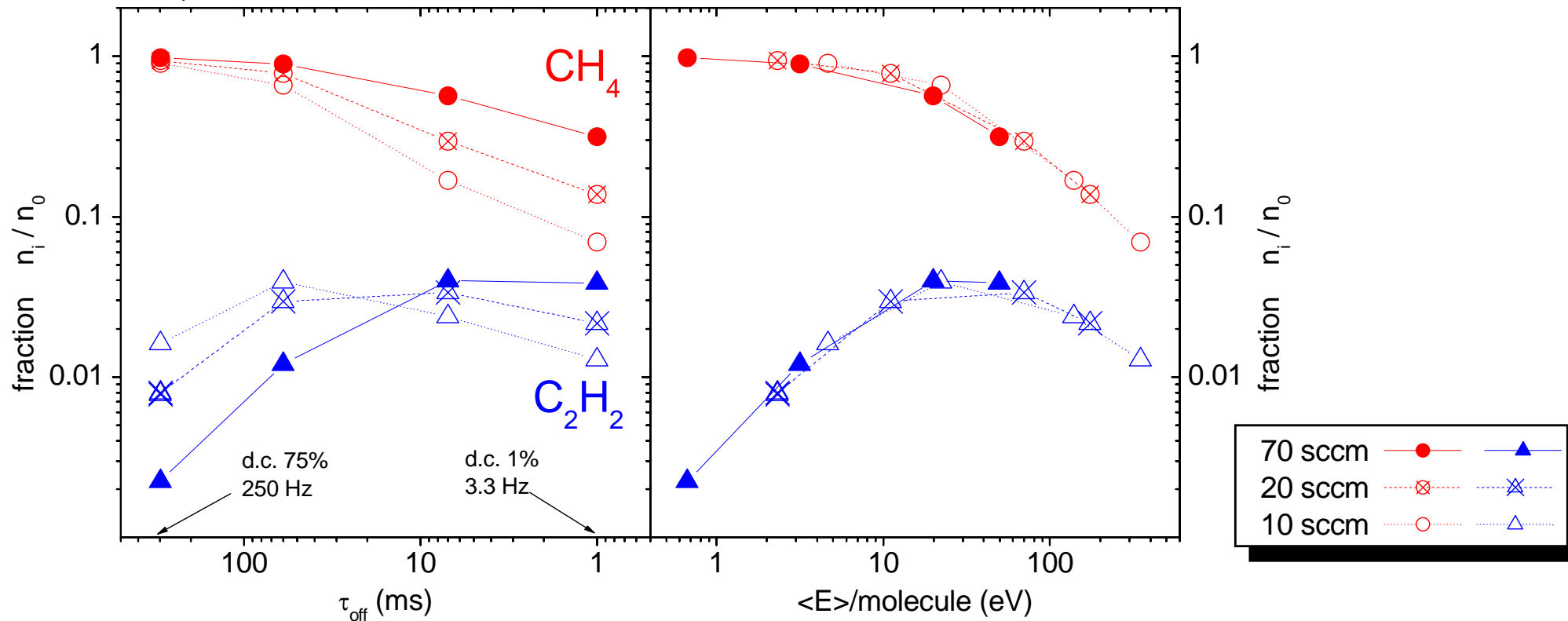
for wide parameter space
in situ in real time







CH₄, 2 Pa, 3 ms on, 300 W



mean energy per source gas molecule:

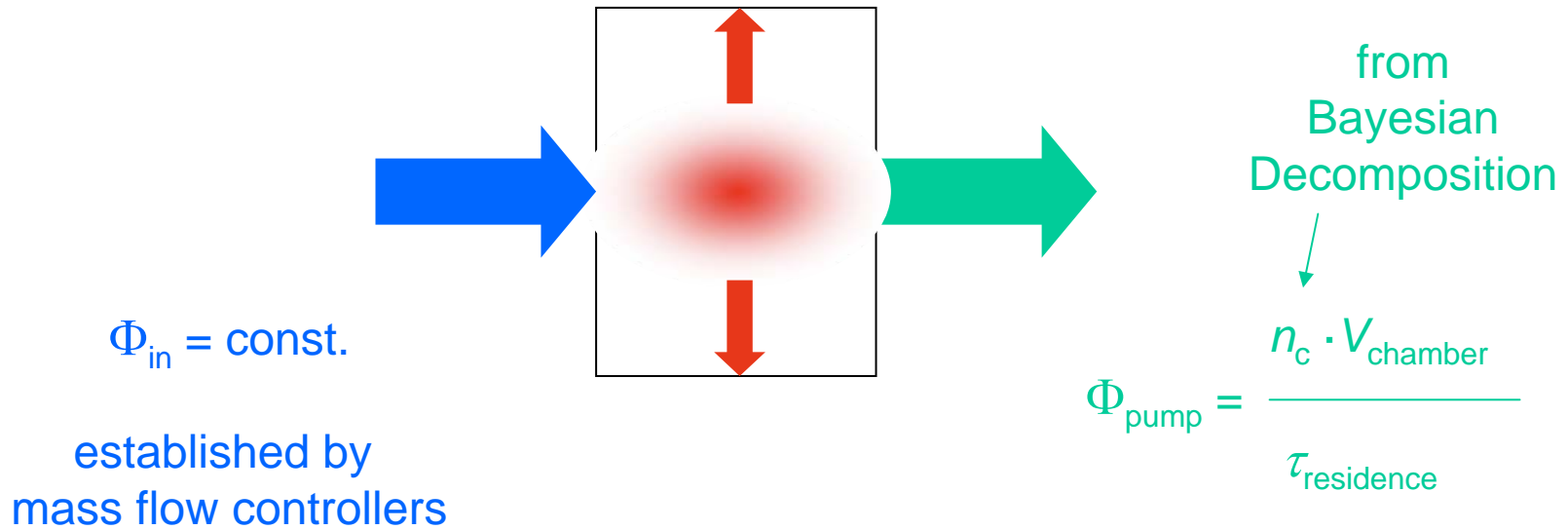
$$\langle E \rangle / \text{molecule} : = E_{\text{mean}} = \frac{P_{\text{mean}} \cdot \tau_{\text{residence}}}{N} = \frac{P_{\text{on}} \cdot d.c.}{N} \cdot \frac{N}{\Phi} = \frac{P_{\text{on}} \cdot d.c.}{\Phi}$$

only valid if:

➤ $\tau_{\text{on}} \ll \tau_{\text{residence}}$

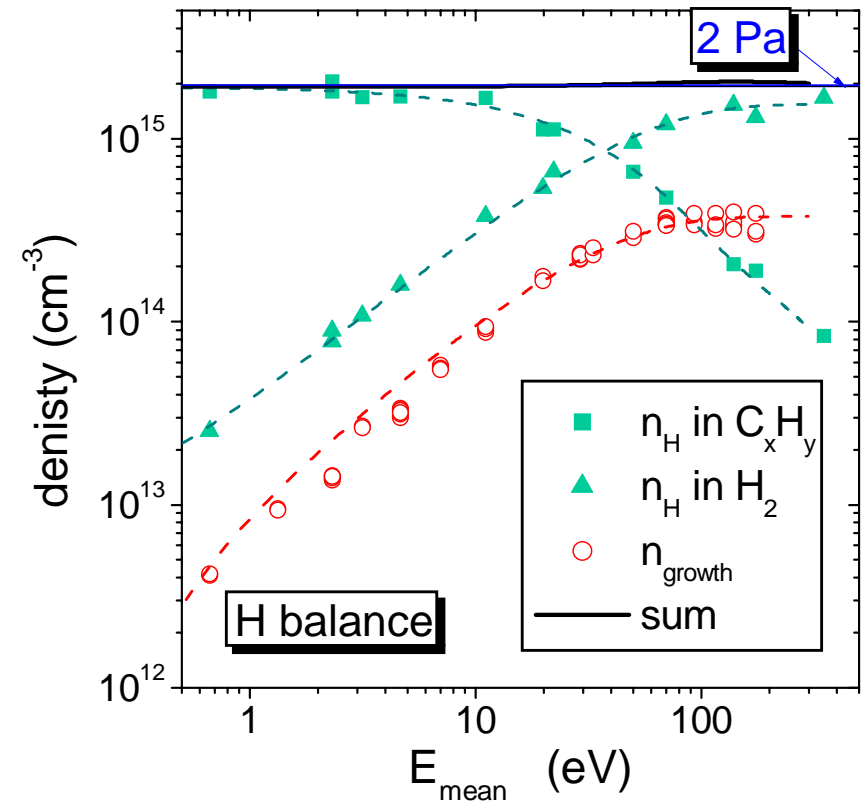
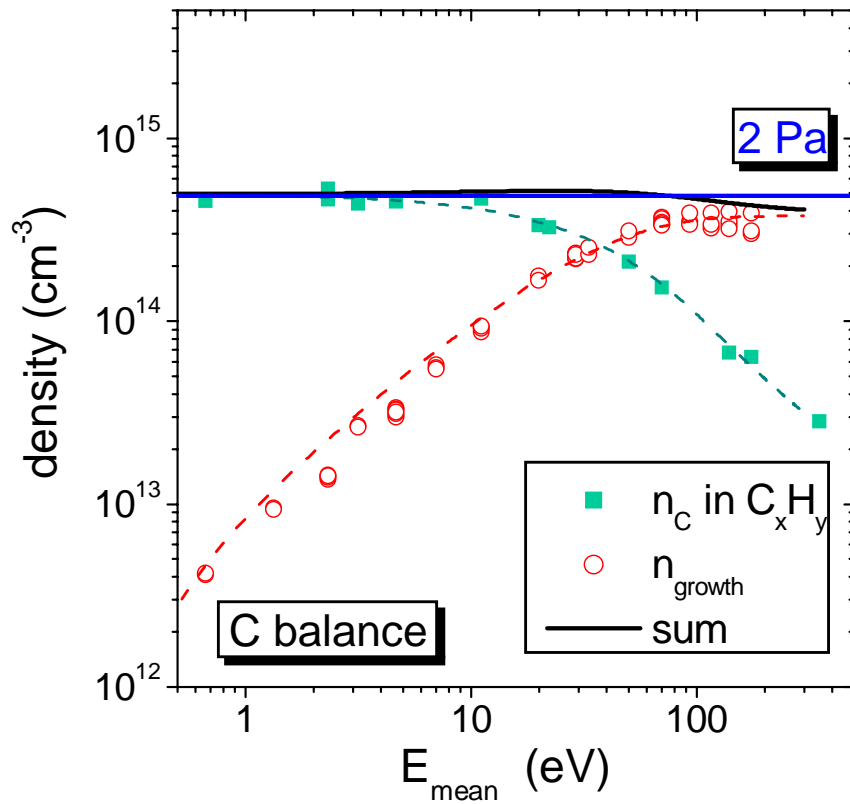
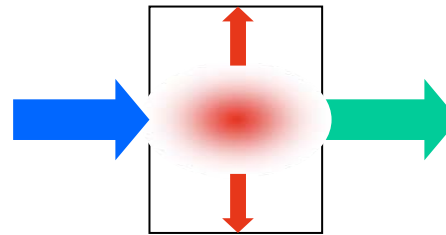
➤ $\tau_{\text{off}} \ll \tau_{\text{residence}}$

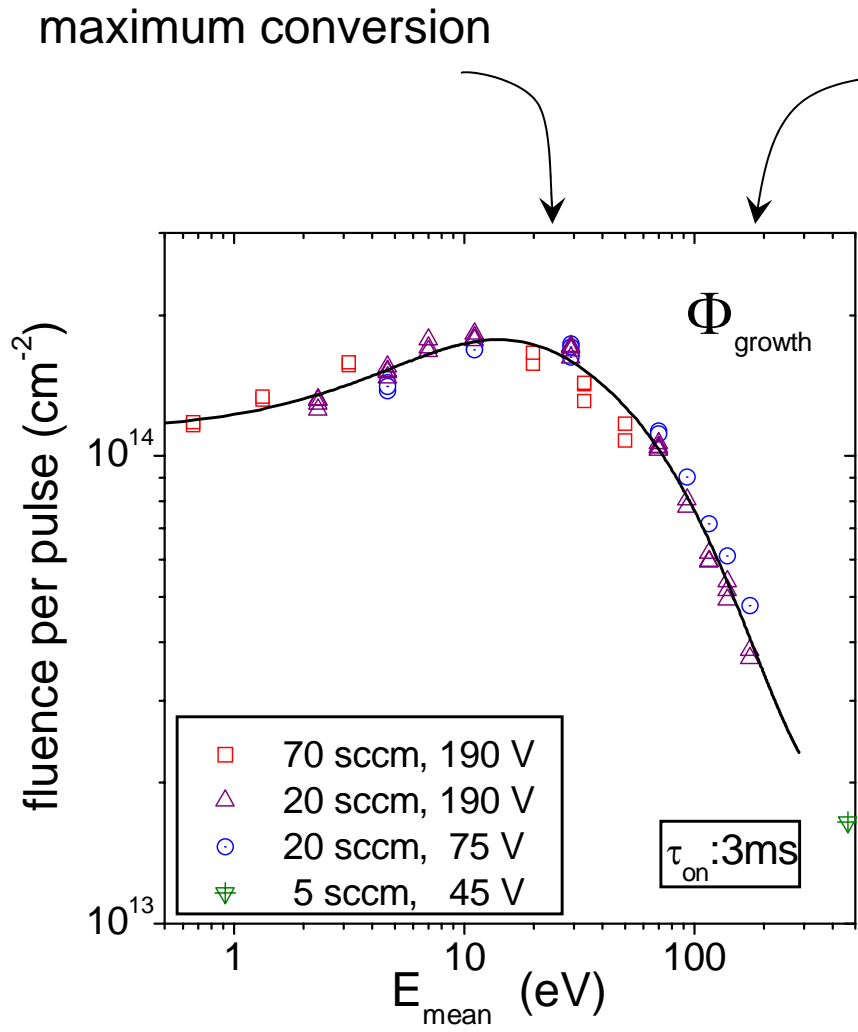
➤ plasma chemistry unchanged



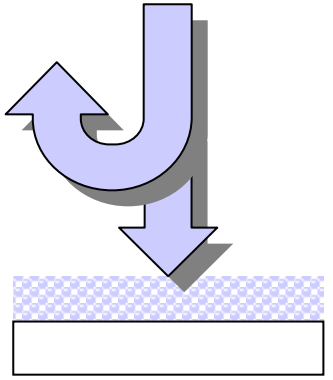
$$\Phi_{\text{growth}} = \Gamma_{C,\text{elli}} \cdot f \cdot A_{\text{plasma}}$$

$\bar{R}_{\text{elli}} \cdot N_c$



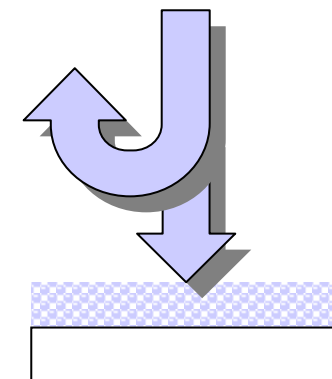
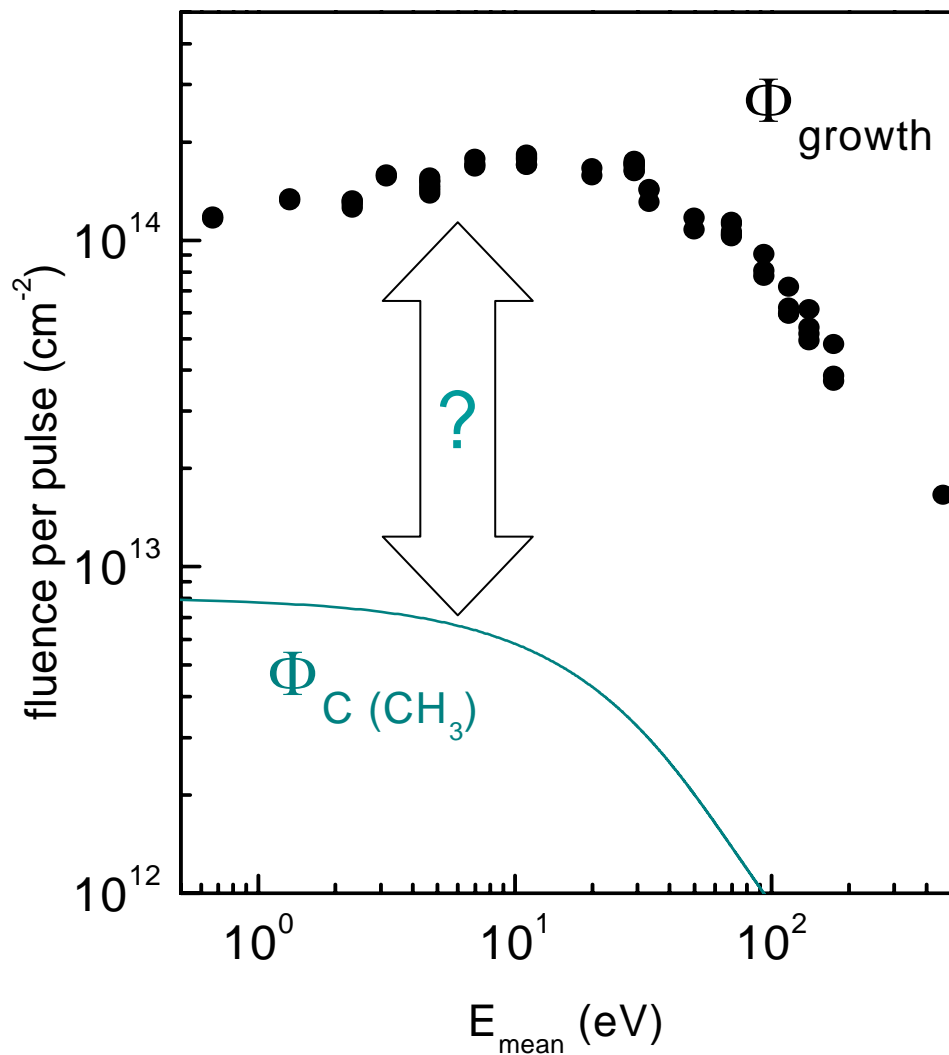


see depletion
in the gas phase



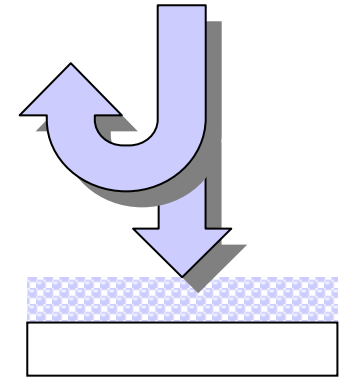
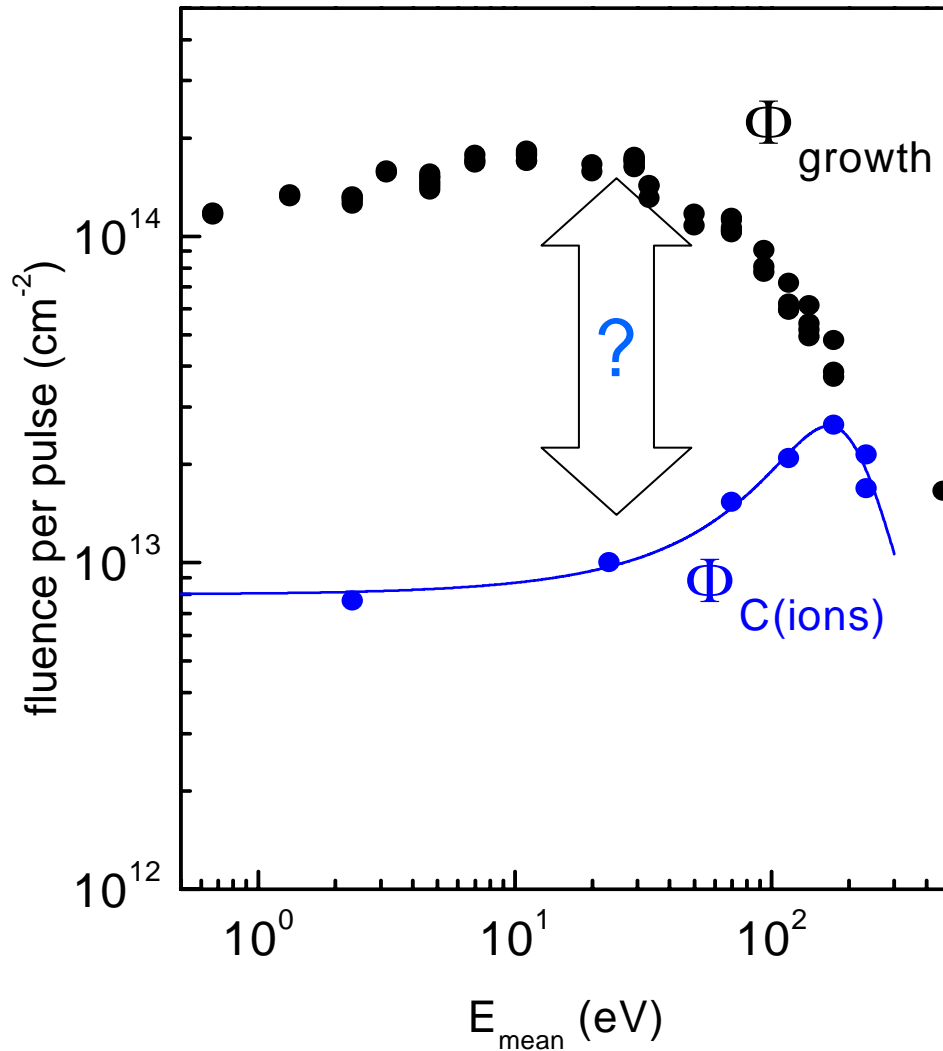
growth fluence:

$$\Phi_{\text{growth}} = \frac{\bar{R}_{\text{elli}}}{d.c.} \cdot N_c \cdot \tau_{\text{on}}$$



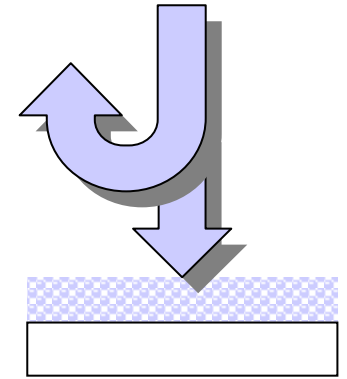
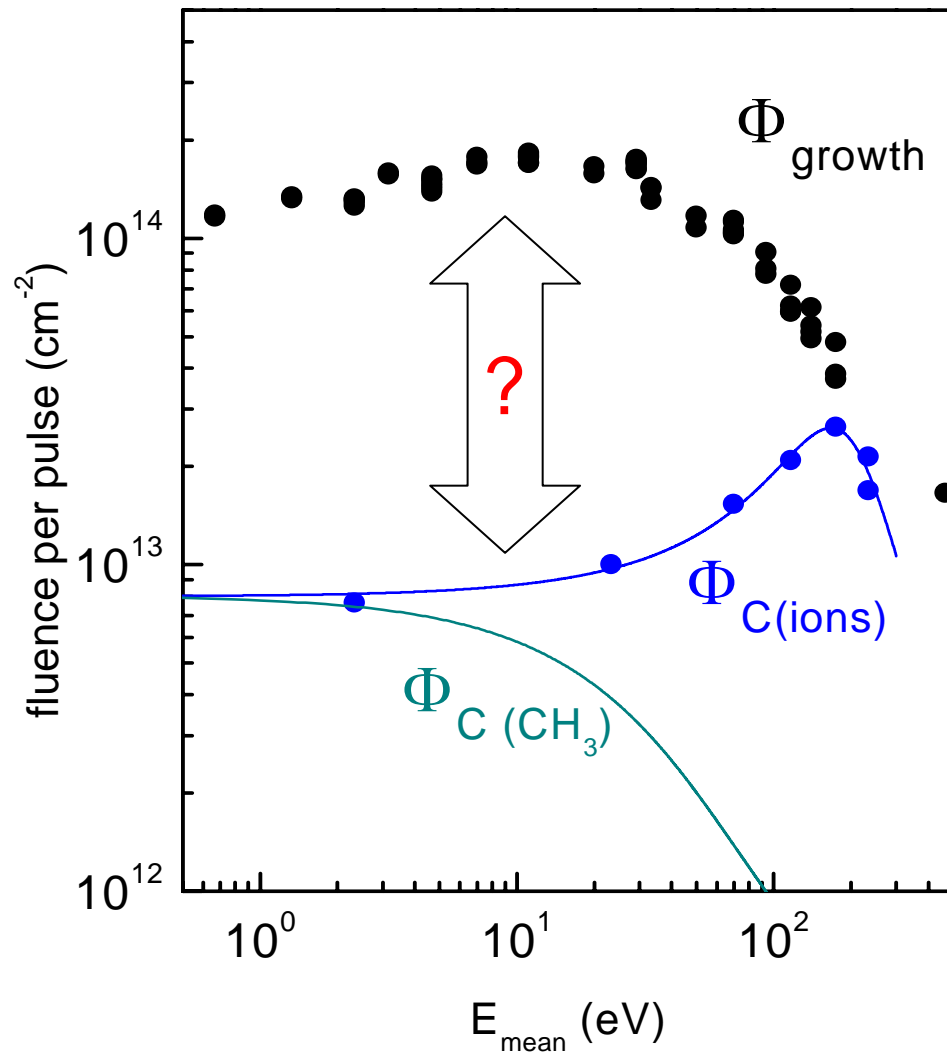
CH₃ cannot explain Φ_{growth}

$$\Phi_{\text{C(CH}_3)} = \frac{1}{4} \cdot n_{\text{CH}_3} \cdot v \cdot \frac{s_{\text{CH}_3}}{1 - \beta_{\text{CH}_3} / 2} \cdot \tau_{\text{on}} \cdot \frac{1}{d.c.}$$



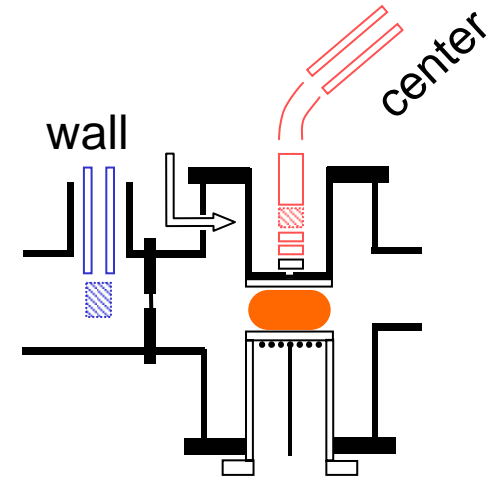
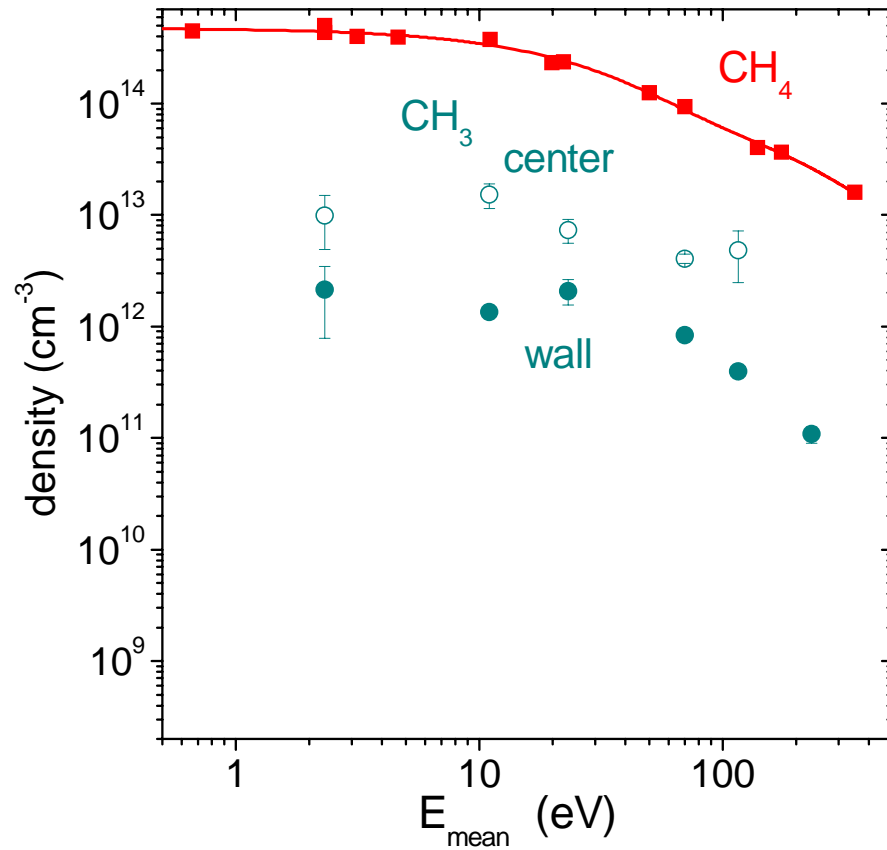
ions cannot explain Φ_{growth}
 (maybe for high E_{mean} they can)

$$\Phi_{\text{C(ions)}} = \frac{\tau_{\text{on}}}{d.c.} \cdot \sum_x s_{\text{C}_x\text{H}_y^+} \cdot j_{\text{C}_x\text{H}_y^+} \cdot x$$

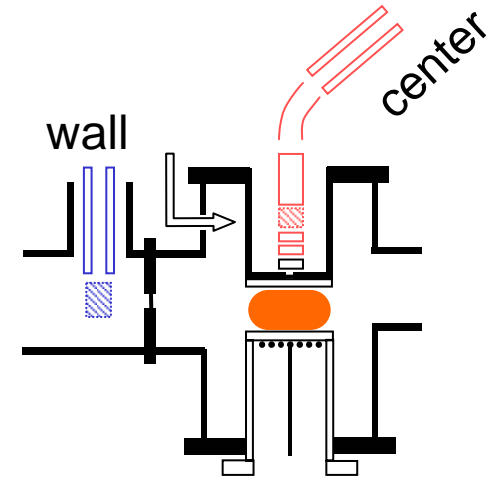
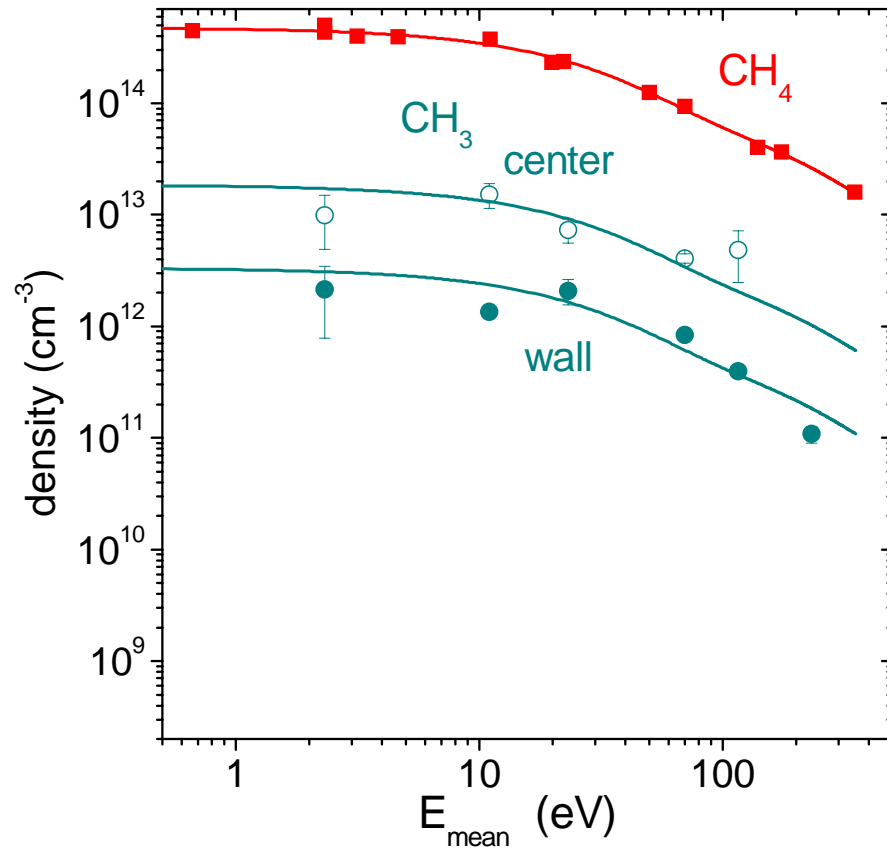


**Growth precursor
from literature
are unable to explain
 Φ_{growth}**

density profile for plasma produced species



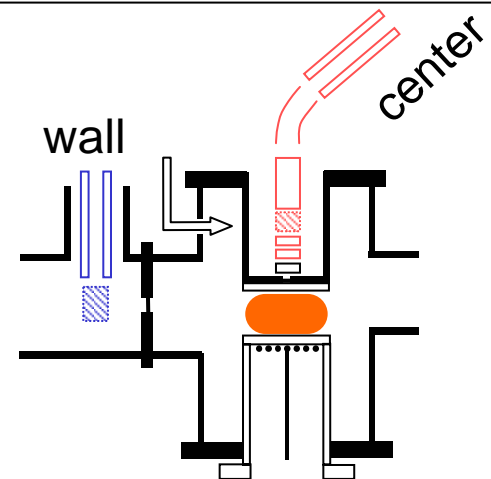
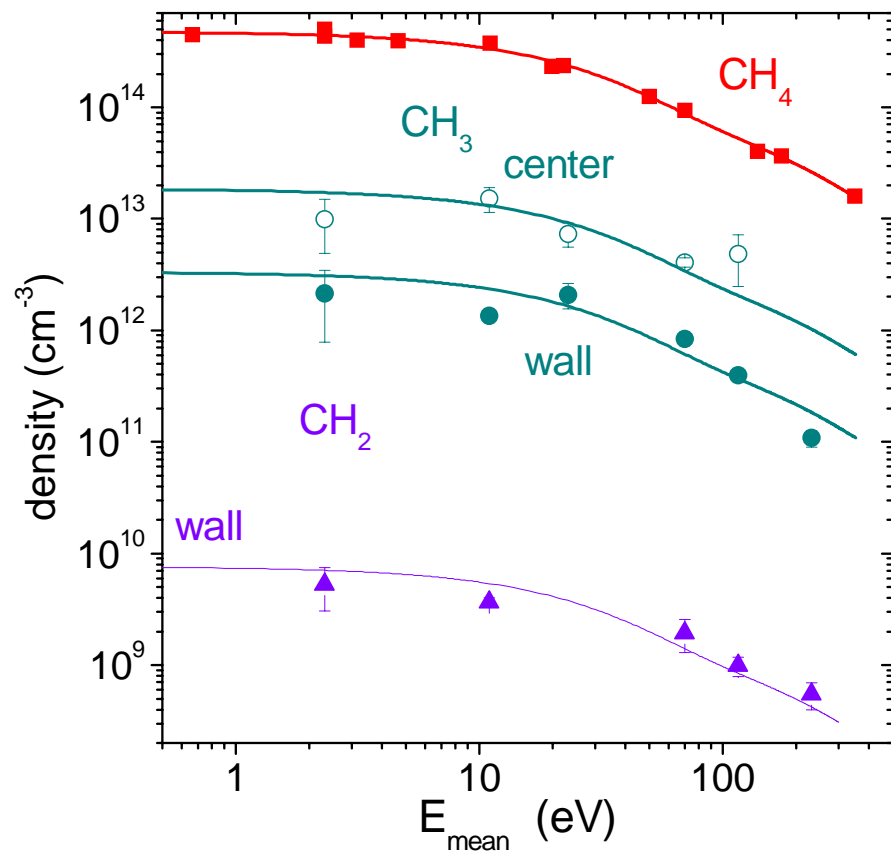
density profile for plasma produced species



observation:

radical production ~ neutral density

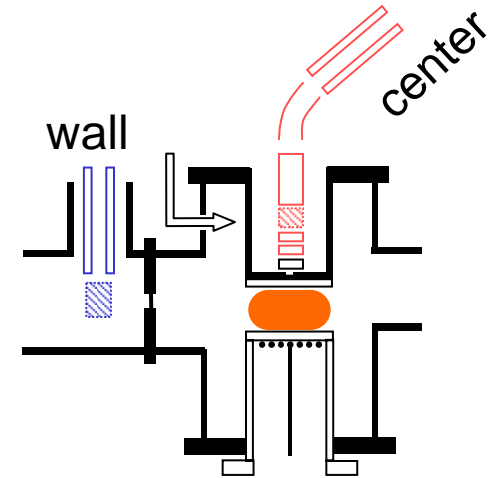
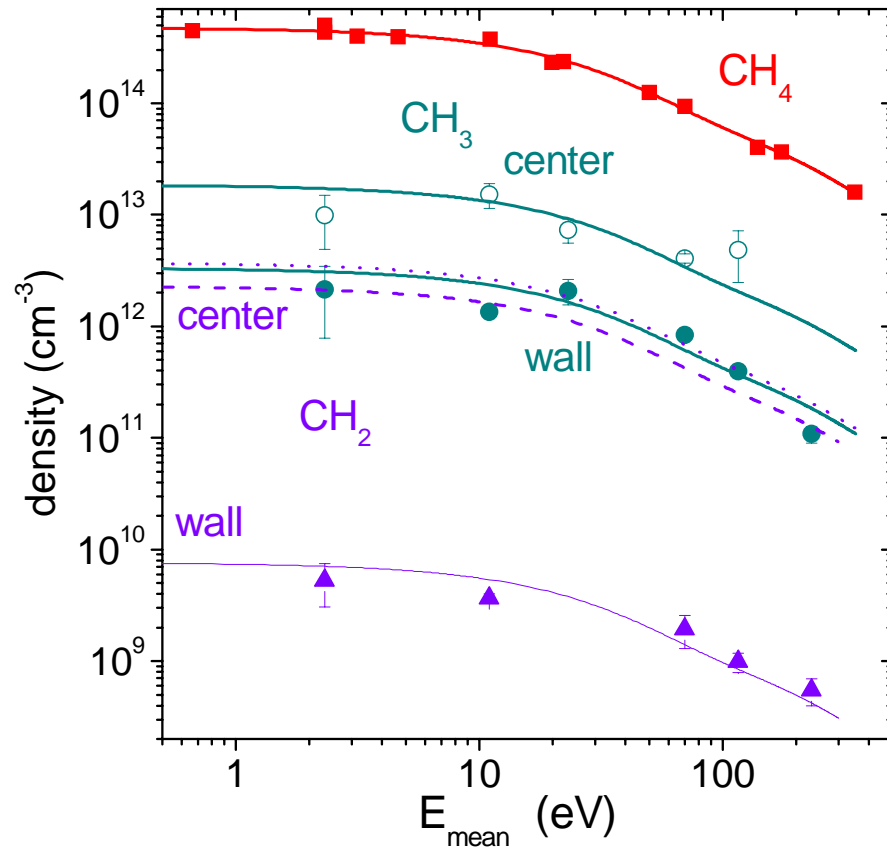
density profile for plasma produced species



observation:

radical production ~ neutral density

density profile for plasma produced species



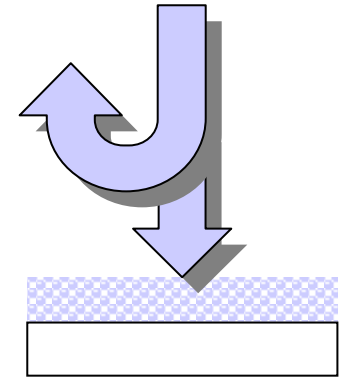
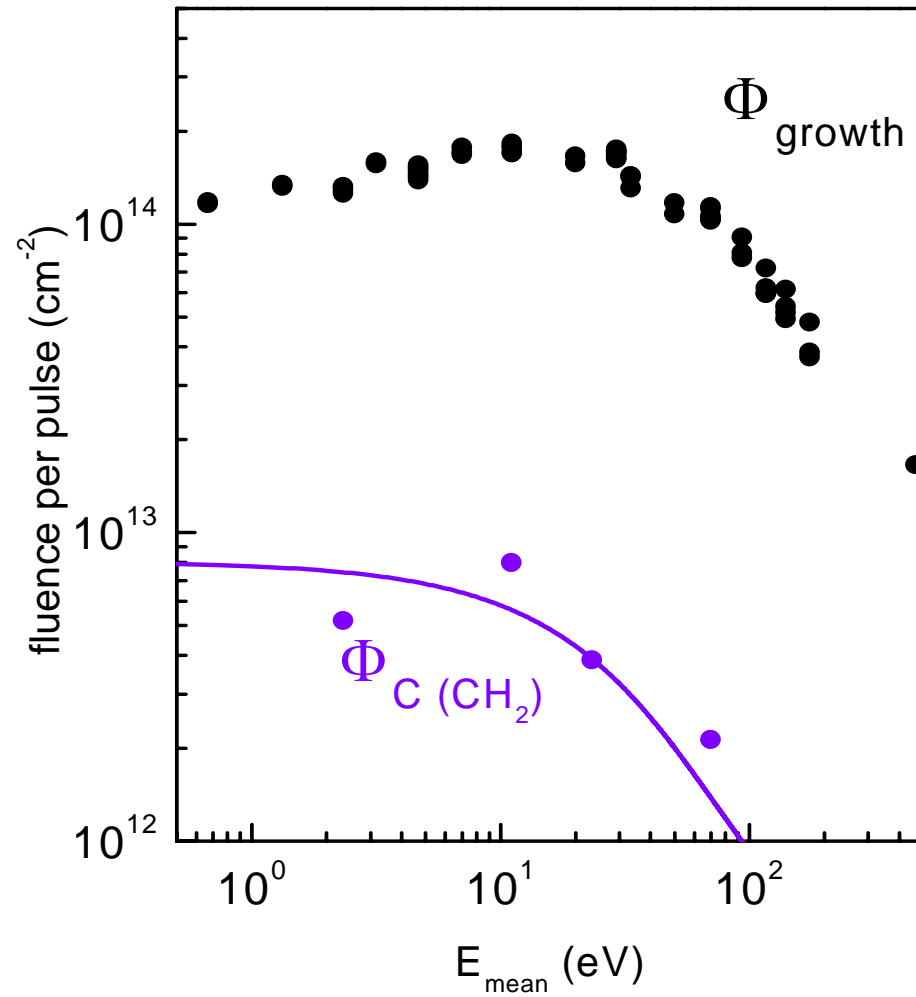
observation:

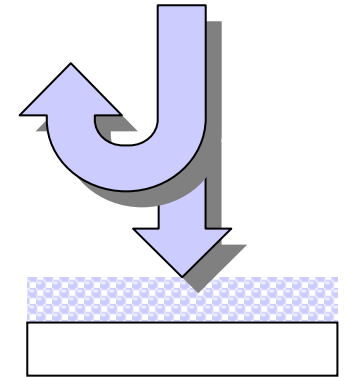
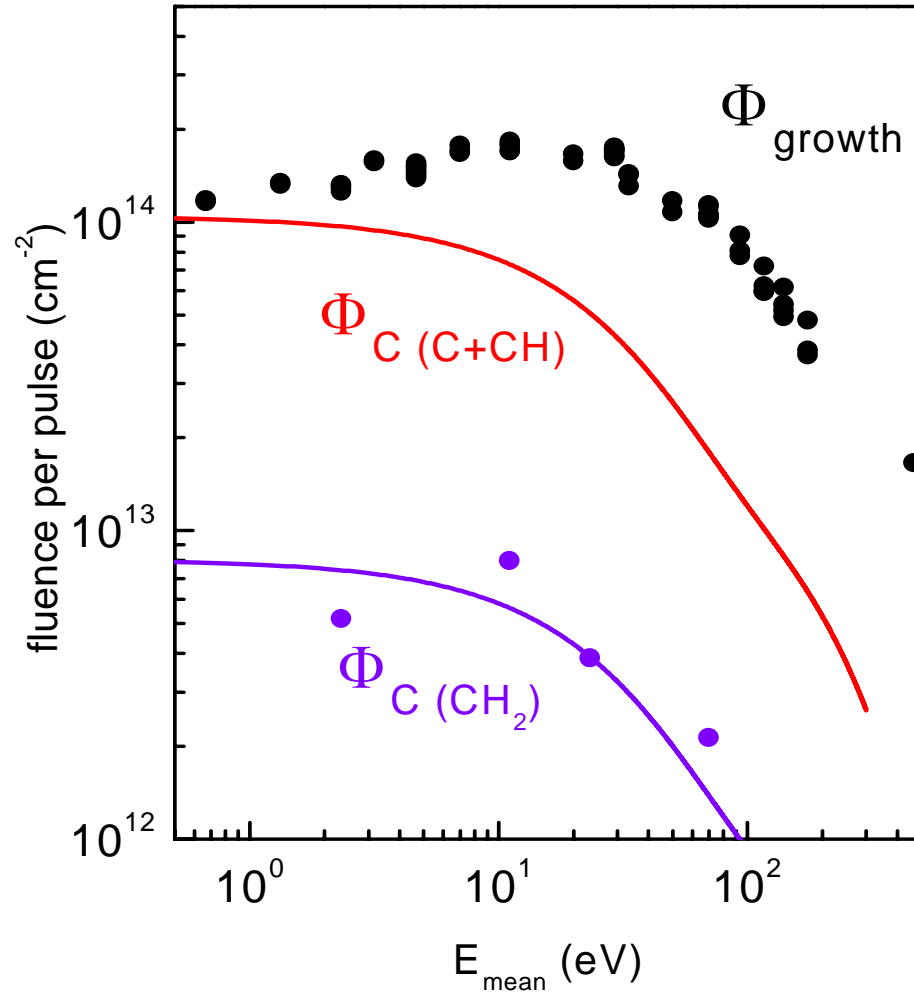
radical production ~ neutral density

therefore: CH_2 and CH from

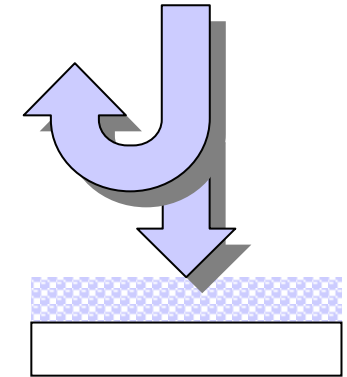
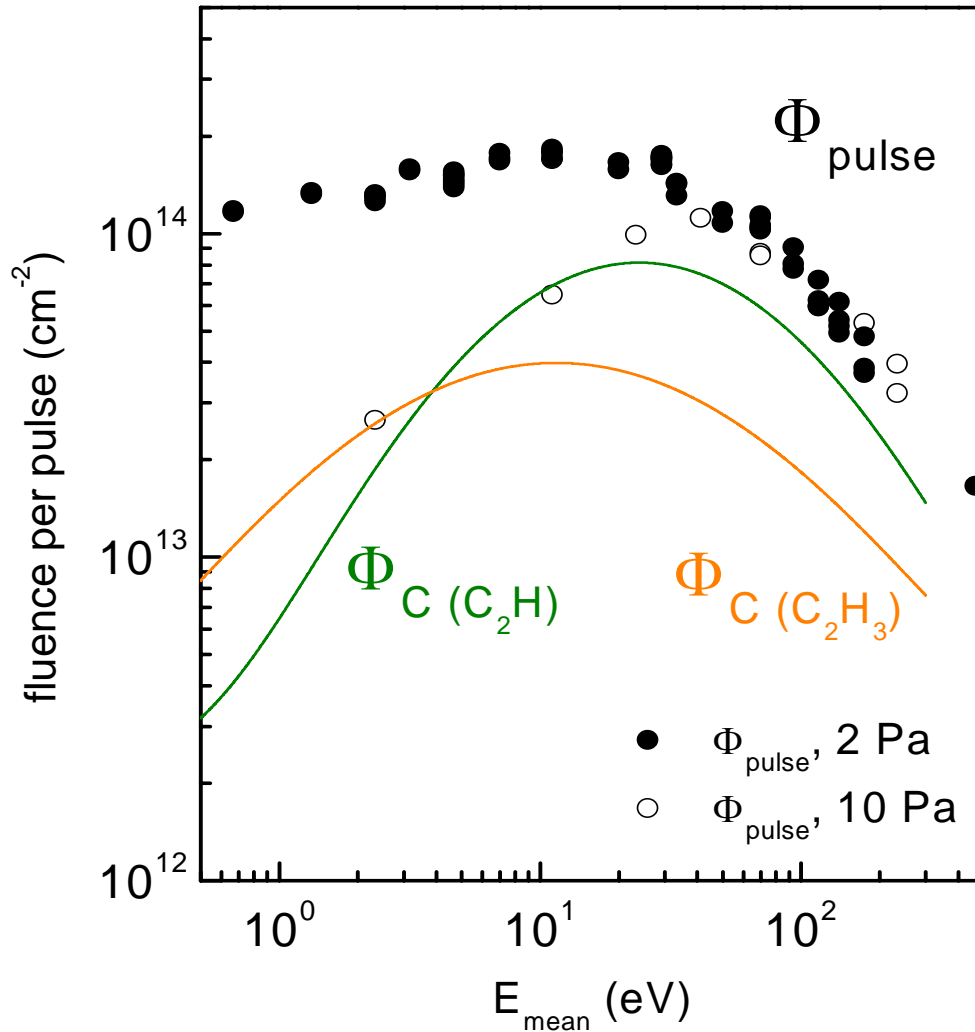
branching ratio ($T_e=3\text{eV}$):

$$n_{\text{CH}_3} : n_{\text{CH}_2} : n_{\text{CH}} : n_{\text{C}} \approx 0.49 : 0.37 : 0.09 : 0.05$$

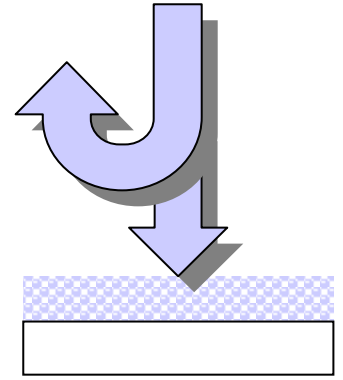
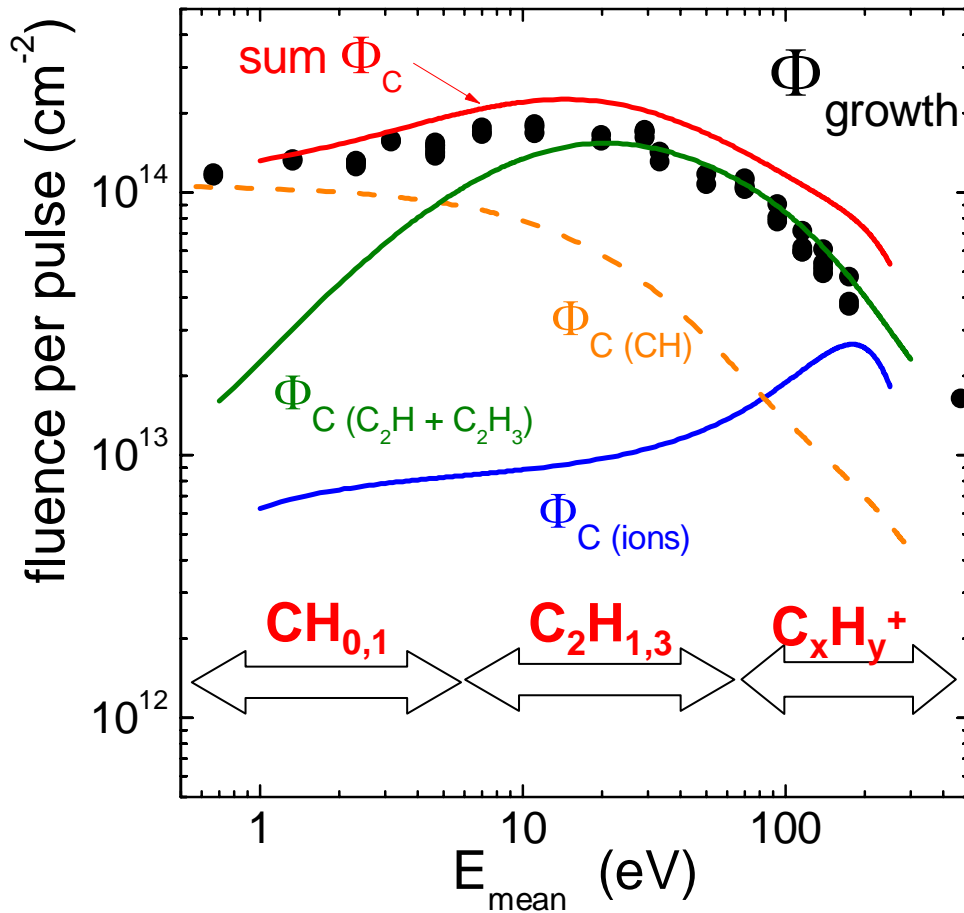




CH_x cannot explain Φ_{growth}



$$\Phi_{C_2H_x} = 2 \cdot n_e \cdot \tau_{on} \cdot \frac{V_{plasma}}{A_{plasma}} \cdot [n_{C_2H_4} \cdot k(C_2H_4 \rightarrow C_2H_3) + n_{C_2H_2} \cdot k(C_2H_2 \rightarrow C_2H)]$$

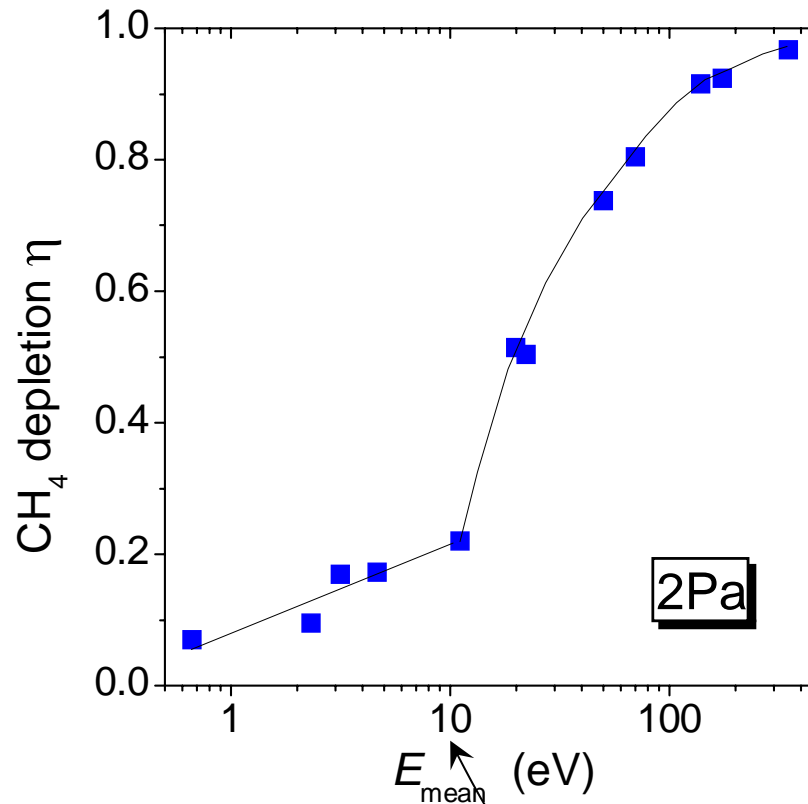


linear superposition of different precursors

- E_{mean} (mean energy per source gas molecule) uniquely determines plasma composition and film growth
- neither CH_3 , nor C_xH_y^+ ions alone can explain film growth
- for $E_{\text{mean}} < 10 \text{ eV}$ C and CH radicals account for growth, CH_2 and CH_3 can be neglected
- for $10 \text{ eV} < E_{\text{mean}} < 100 \text{ eV}$ C_2H and C_2H_3 radicals dominate film growth, growth per pulse peaks around 20 – 50 eV
- for $E_{\text{mean}} > 100 \text{ eV}$ ions become significant, hydrogen dominates, source gas depletion

source gas depletion:

$$\eta(E_{\text{mean}}) = 1 - \frac{n_{\text{CH}_4}(E_{\text{mean}})}{n_{\text{CH}_4}(0\text{eV})}$$



dissociation energy for CH₄:
8.8eV

ellipsometry allows to determine the optical constants n , κ and d with great accuracy

for a-C:H powerful quantitative tool because:

total growth rate (carbon atoms / area / time)

can be determined because of strong correlation

between density and refractive index

