‘Etching/deposition’ and molecular growth in discharge plasmas

Discharge dynamic / plasma chemistry / plasma surface interaction

LIMHP group (HC discharges : particle formation and film deposition)

F. Silva[1], G. Lombardi[1], F. Mohasseb, A. Michau[1], X. Bonnin[1], X. Duten, F. Benedic, K. Hassouni, J. Achard and A. Gicquel[1]

PIIM group (carbon particle formation)

C. Arnas

PICM group (Si-H discharge and Si-H particles formation)

H. Vach and N. Ning

Outline

Objective : to illustrate some of the approaches used to investigate plasma surface interaction, molecular growth and particle formation in plasma process

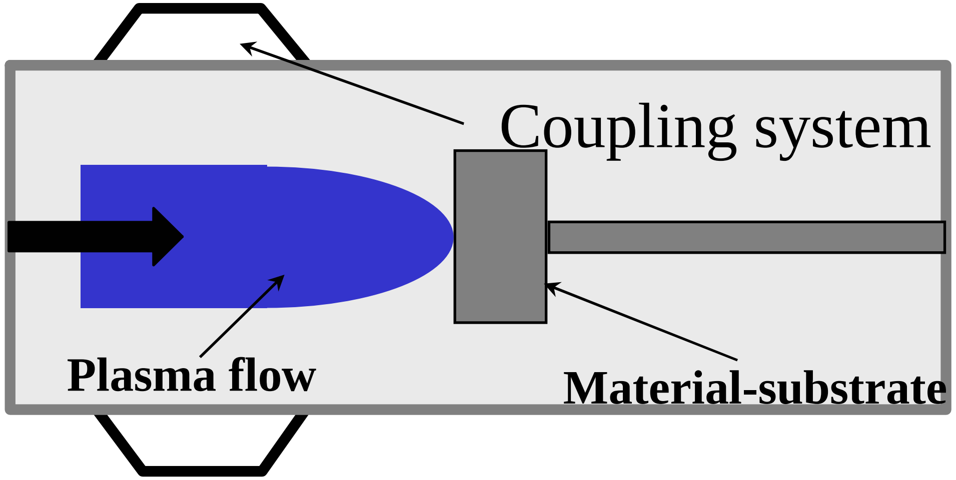
➔ **Plasma physisist / Data user point of view**

- **Neutral plasma species implication in :**
  - **surface process : the case of diamond deposition**
  - **molecular growth : the example of soot formation in HC discharges**

- **Sputtering and negative ions implication in :**
  - **➔ Particle generation and dusty plasma formation**
  - **➔ The case of graphite cathode DC sputtering**

- **Negative ions and molecular growth in plasma**
  - **➔ Hydrogen and SiH_4 dusty plasmas**

Laboratory discharge plasmas
The chemical species involved



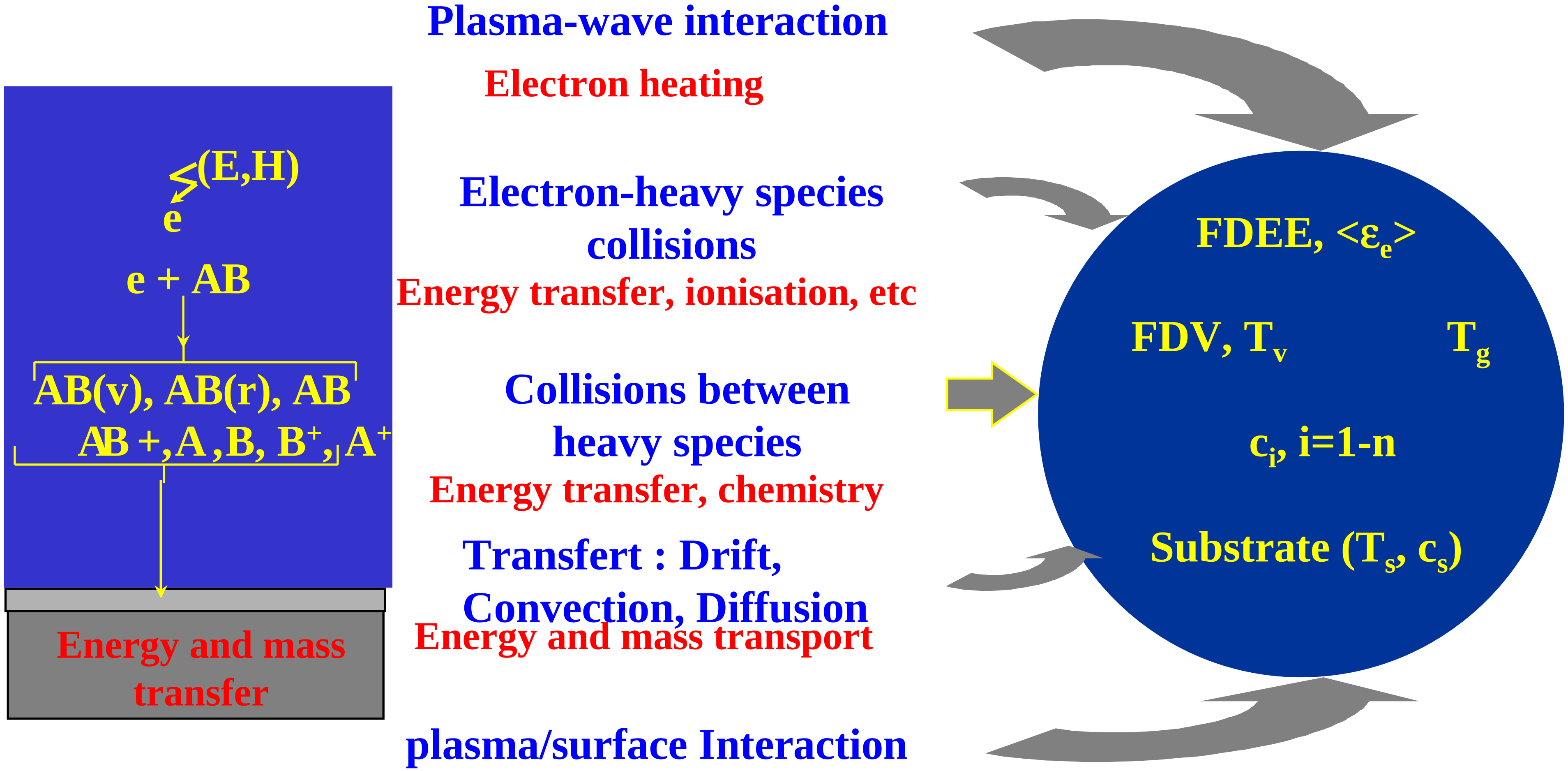
Discharge conditions :
- Pressure : 0.1-10^5 Pa
- Input-Power : 1 – few 10^3 W
- τ_s : 10^{-3}-qqs sec

-$Pe_n < 10$, $Re_{gaz} < 100$
-Power density : 10^{-3}-10^3 W/cm^3

Some orders of magnitude :

* $n_e = 10^8$-10^{14} cm^{-3} ($<10^{-2}$ and more often $<10^{-5}$)
* $<\varepsilon_e> = 1$-10 eV
* $T_g = 300$ - 6000 K
* 'T_v' = 1000 - 5000 K (molecular gases)

Plasma/surface interaction : The context



(E,H)
e

e + AB

AB(v), AB(r), AB

AB +, A , B, B$^+$, A$^+$

Energy and mass transfer

Plasma-wave interaction

Electron heating

Electron-heavy species collisions

Energy transfer, ionisation, etc

Collisions between heavy species

Energy transfer, chemistry

Transfert : Drift, Convection, Diffusion

Energy and mass transport

plasma/surface Interaction

Energy and mass transfer

FDEE, $<\varepsilon_e>$

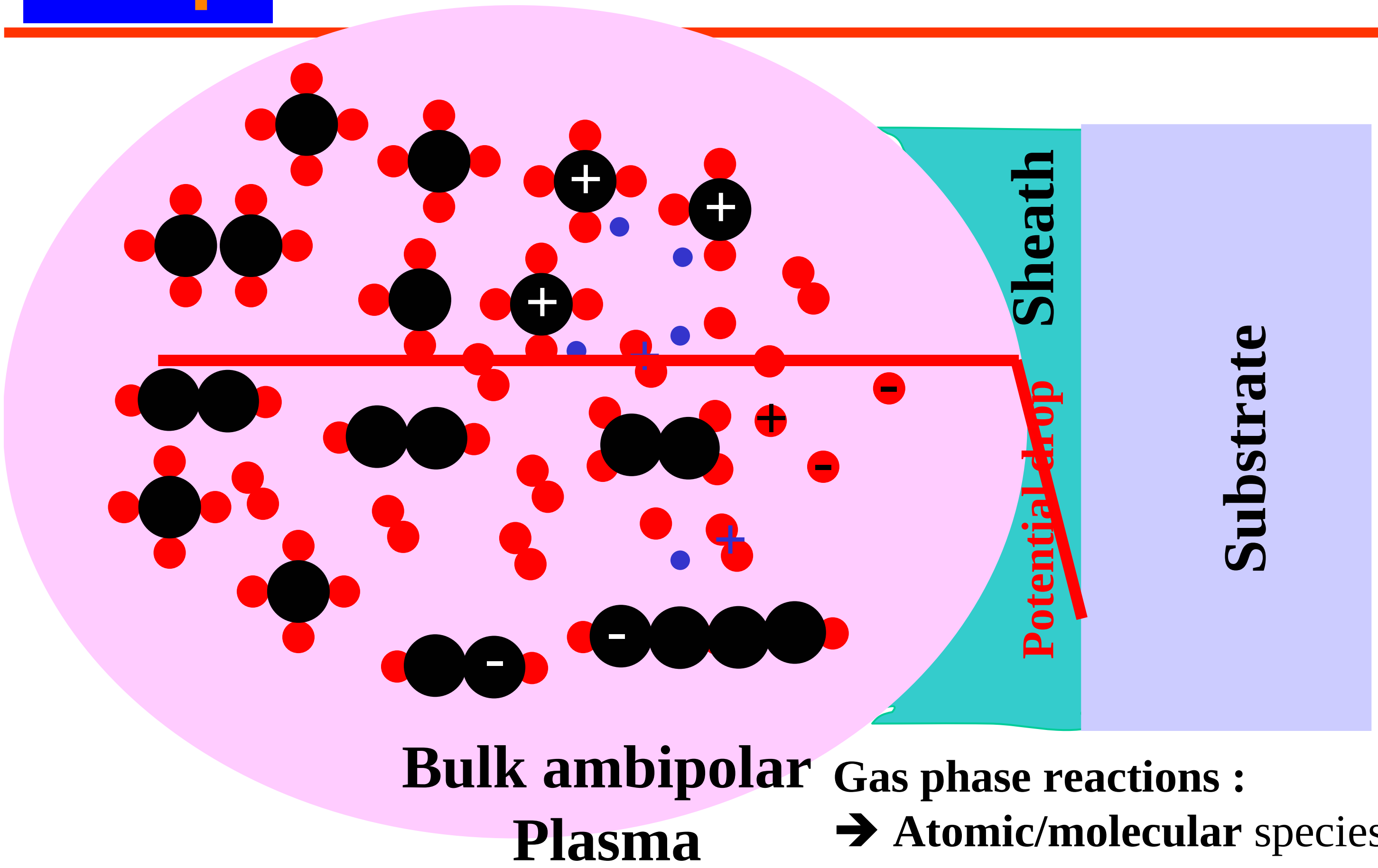
FDV, T_v

T_g

c_i, i=1-n

Substrate (T_s, c_s)

Plasma/surface interaction : Gas phase generated species



⬤ = C or Si

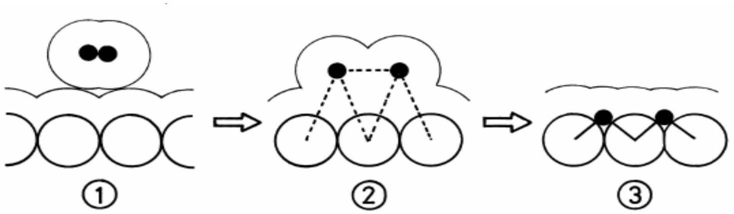
● = H, O, F, Cl

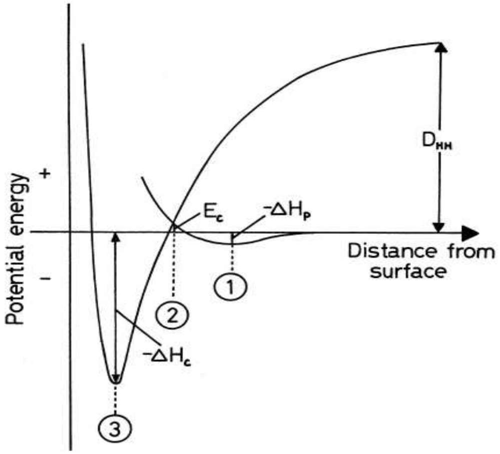
• = electron

Gas phase reactions :

- ➔ **Atomic/molecular** species : O-atom, F-atom, H-at
- ➔ Radicals : CH_3, CF_3, SiH_2, SiH, SiH_3
- ➔ Positive ions : CH_5^{+}, SiH_5^{+}, H_2^{+}, H_3^{+}, H^{+}, O_4^{+}, etc.
- ➔ Negative ions : H^{-}, O^{-}
- ➔ Large molecular structures : $S_nH_m^{-}$, $C_nH_m^{-}$, etc.

Plasma/surface interaction :
Gas phase generated species = neutral





Gas phase generated neutral (atoms and radicals) :

In the bulk :

Birth :

Electron-impact dissociation on the parent molecules

Energy threshold : 4-10 eV

Transport : free diffusion ➔ **low drift energy**, thermal species ➔ **isotropic fluxes**

Fate on the surface ➔ ***soft* chemistry** : adsorption, recombination (L-H, R), chemisorption, **etching** ($A_g + B_s \rightarrow C_g$)

In the sheath:

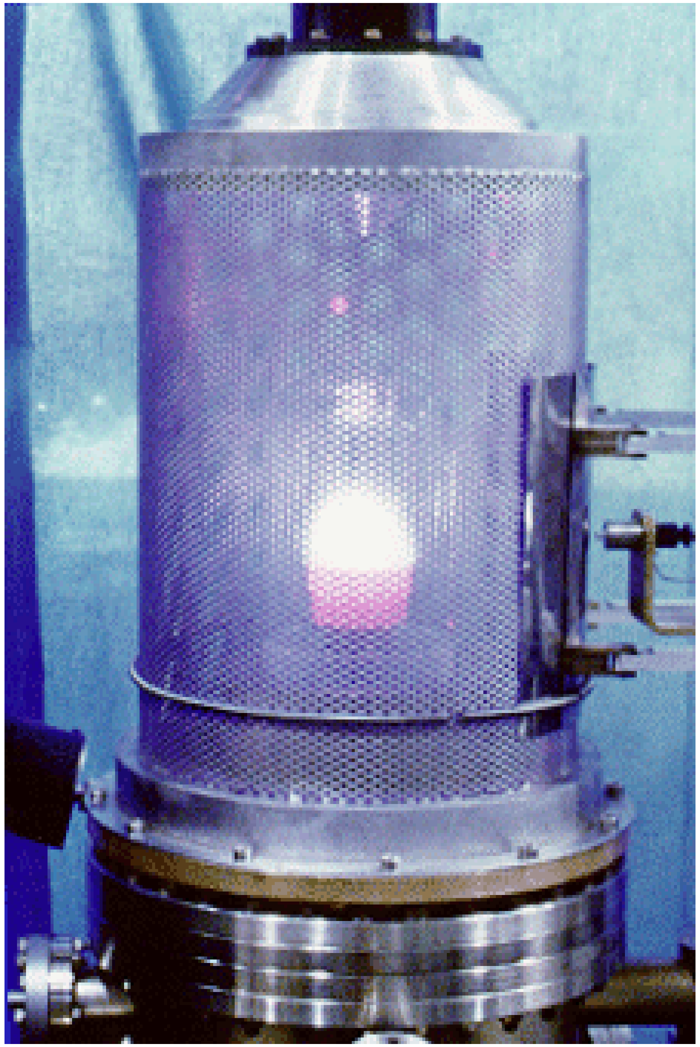
Birth : charge transfer : « **hot atoms** , neutrals »

Resonant process : $\mathbf{Ar^+_{fast} + Ar \rightarrow Ar_{hot} + Ar^+_{slow}}$

Transport : free diffusion, high energy neutral = $10\text{-}10^3$ eV

Fate : surface soft chemistry : adsorption, recombination (R), chemisorption, etching, and **also sputtering**

Neutral species driven Plasma-surface interaction The example of diamond deposition



ν *Bell Jar Reactor type*

- *2-6 kW*
- *P=25-200 mbar*

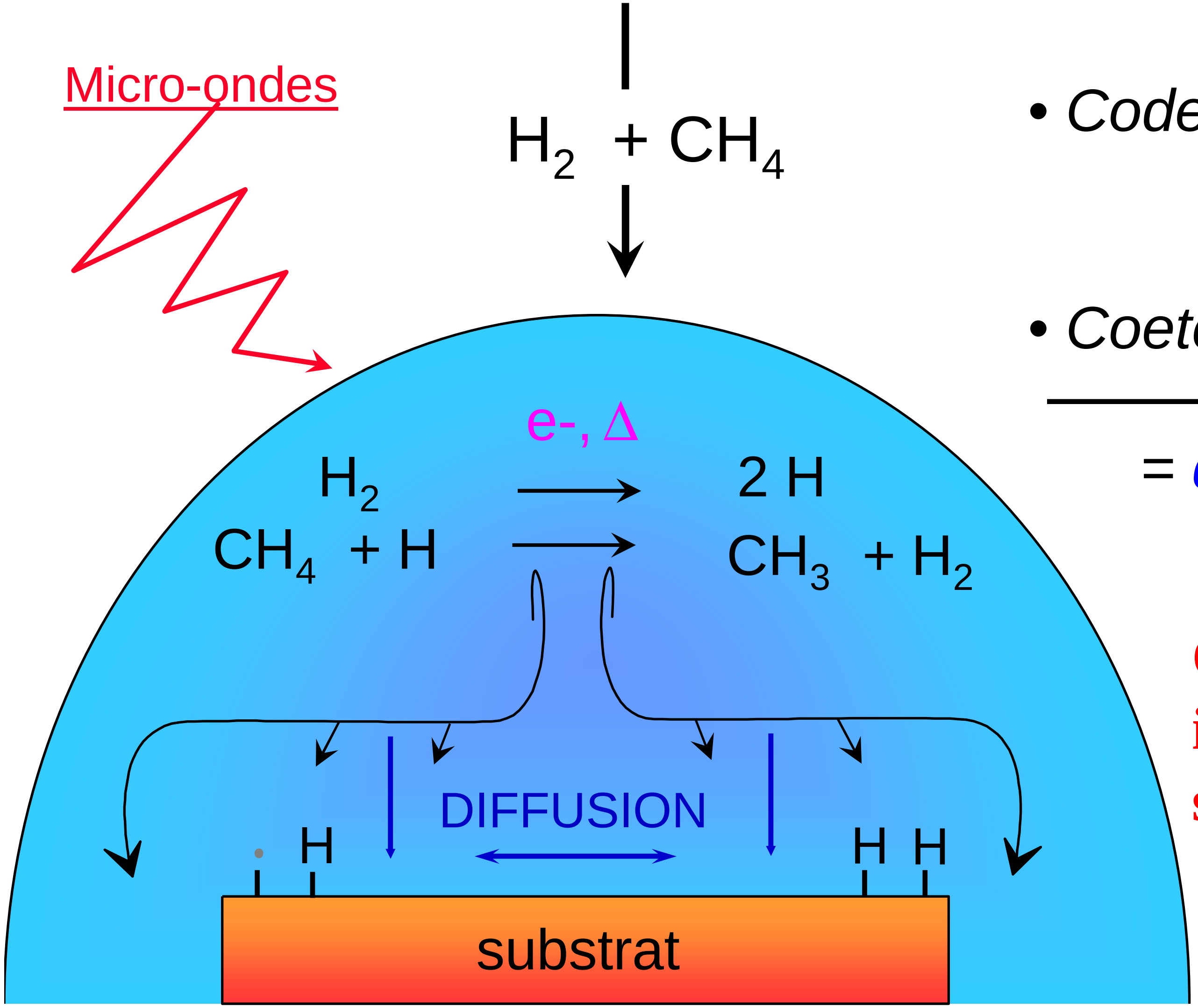
ν *Deposition parameters*

- *%CH_4 : 0.25 - 16 %*
- *Ts : 400 - 1000°C*
- *dP_{MW} : 9 - 30 W/cm^3*
- *t : 0.5 - 600 h*

Sheath

few tens of microns
totally collisional for ions
very small potential drop (floating)
➔very low energy ions
➔Low ion flux (vs atom and radicals)

PACVD of diamond principle



Micro-ondes

$H_2 + CH_4$

e^-, Δ

$H_2 \longrightarrow 2\,H$

$CH_4 + H \longrightarrow CH_3 + H_2$

DIFFUSION

· H

H H

substrat

- *Codeposition of* (sp_2, sp_3)

+

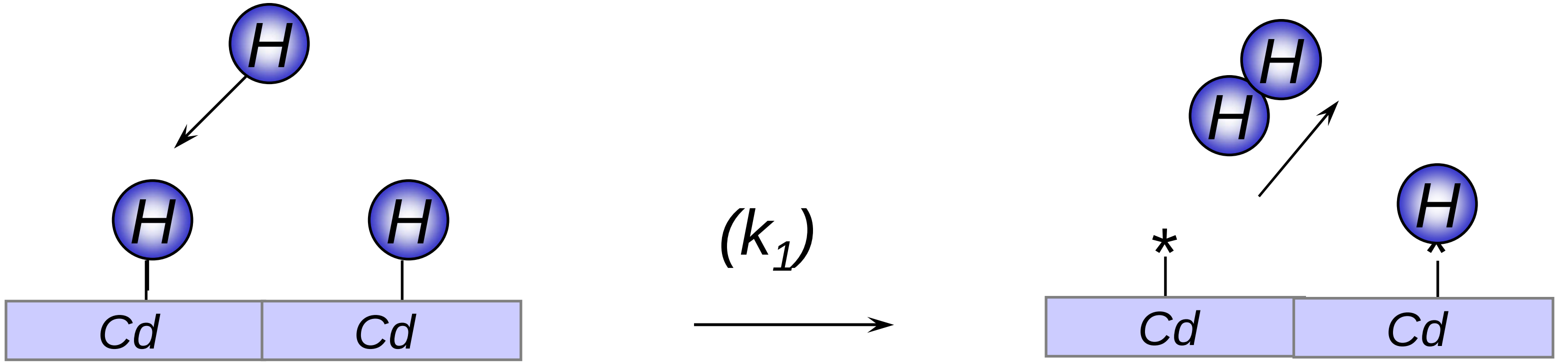
- *Coetching* (sp_2, sp_3)

= *diamant polycristallin*

Only neutral chemistry involved in the plasma surface interaction

Diamond growth ; purely neutral mechanism
Key-role of H-atom adsorption ⇔ recombination equilibrium

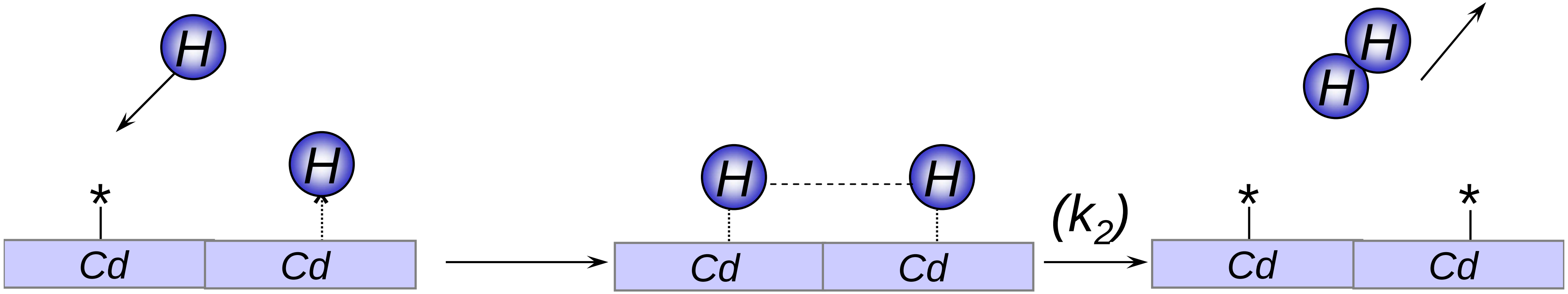
Rideal mechanism



$\gamma_H \approx 10\ \%$ (1000 K)-

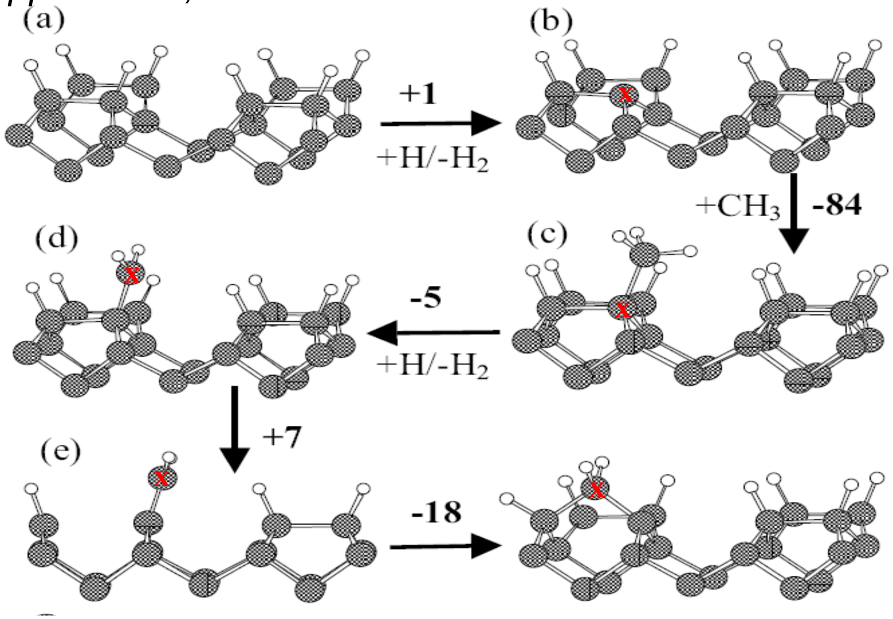
active site : Cd*

Langmuir-Hinshelwood

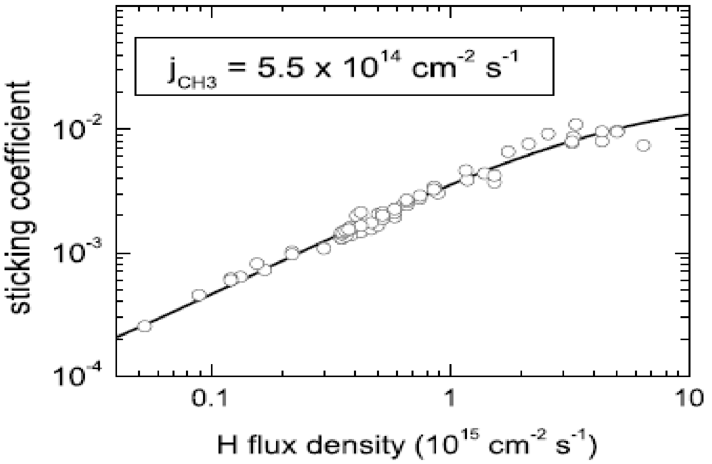


Adsorption-Recombination assisted growth of diamond CH_3 as growth precursor (Goodwin model)

From P. Zapol,a L. A. Curtiss,a H. Tamura,b and M. S. Gordon
Computational Materials Chemistry: Methods and Applications, 266–307.



From : W. Jacob, C. Hopf, M. Meier, and T. Schwarz-Selinger in Springer Series in Chemical Physics (2005)Volume 78



H-atom ➔ growth rate

Plasma physisist :
How much CH_3 stick to my surface ?
(what are my boundary conditions ?)

Surface scientist answer :
It depends on the H-atom flux your plasma delivers

==> Neutral-neutral synergetic effect

==> non linear surface chemistry

The simplest and most succesfull Diamond growth model

$$Cd - H + H \xrightarrow{k1} Cd^{*} + H_2$$

$$Cd^{*} + H \xrightarrow{k2} Cd - H$$

$$Cd^{*} + CH_3 \underset{k4}{\overset{k3}{\rightleftarrows}} Cd - CH_3$$

$$Cd - CH_3 + H \xrightarrow{k5} Cd - CH_2^{*} + H_2$$

$$Cd - CH_2^{*} + H \xrightarrow{k6} Cd - Cd - H$$

H-atom is a key-species

Growth rate derived from Goodwin model
Growth is function of H-tom flux

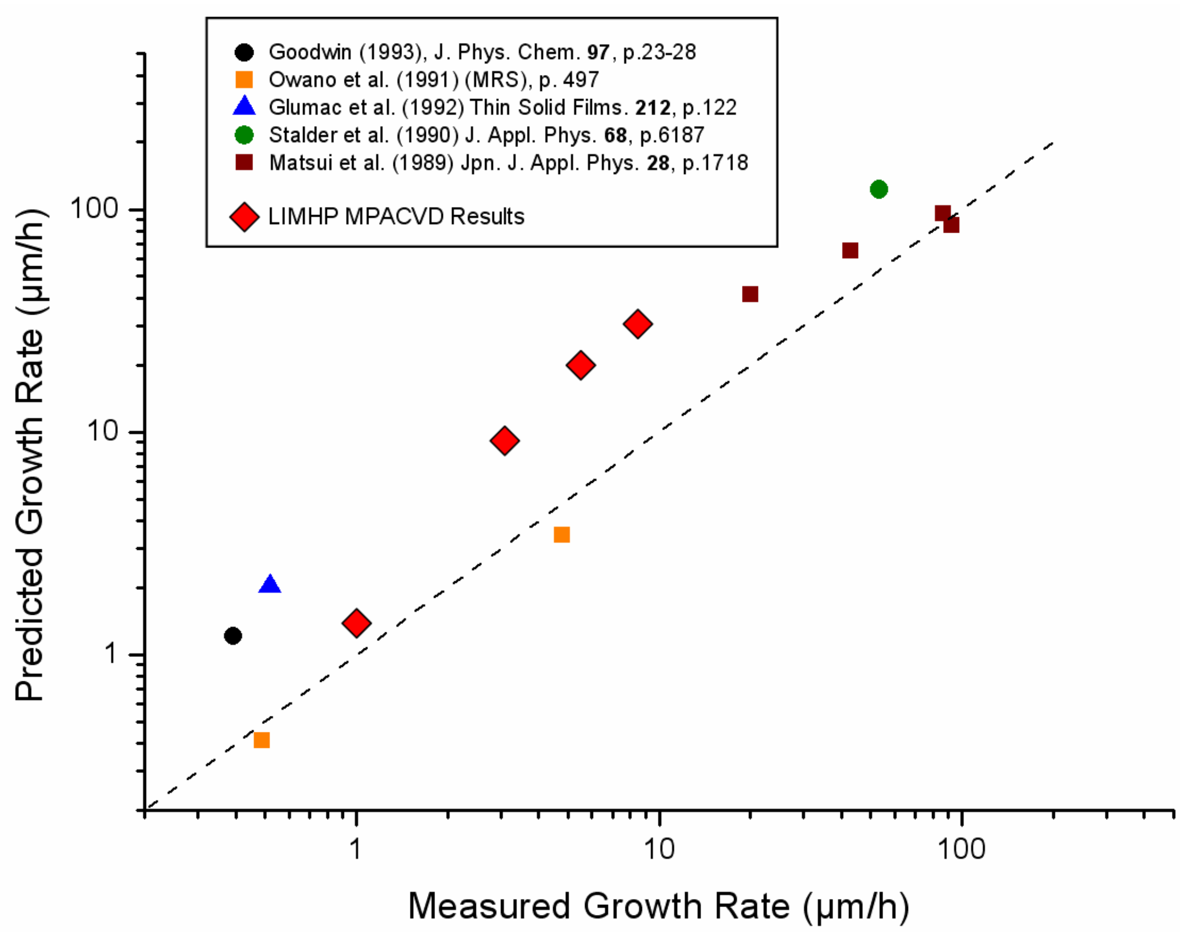
Surface concentrations

Site density

$$G_{100} = k_3 \frac{n_s}{n_d} \left(\frac{k_1}{k_1 + k_2} \right) \frac{[CH_3]_s . [H]_s}{\frac{k_4}{k_5} + [H]_s}$$

Diamond density

Growth rate derived from Goodwin model
Growth is function of H-tom flux

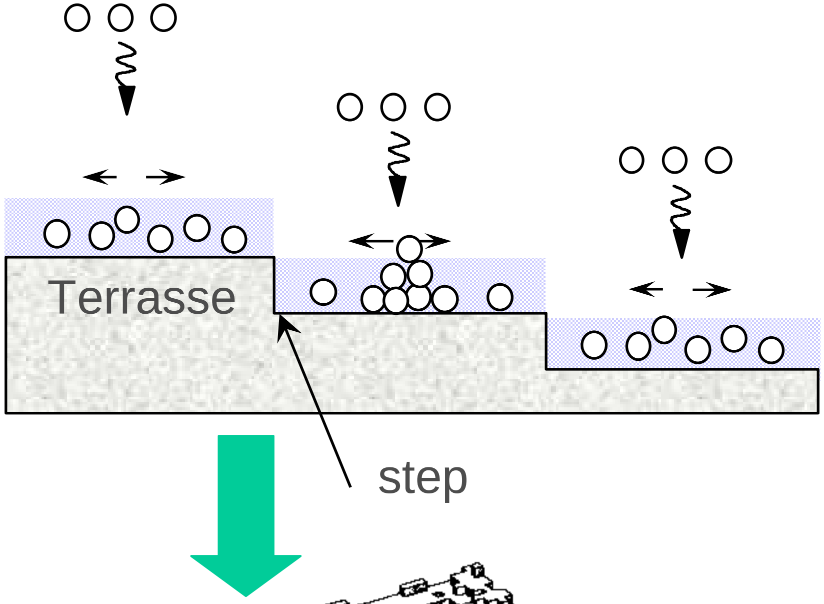


Diamond growth –mesoscale – what are the observable growth mechanism Nucleation growth

- High flux of the precursor species

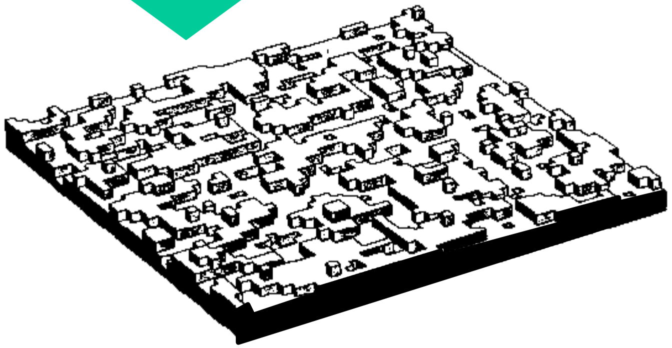
Diffusion length << terrasses length :

Nucleation of 2D islands on terrasses



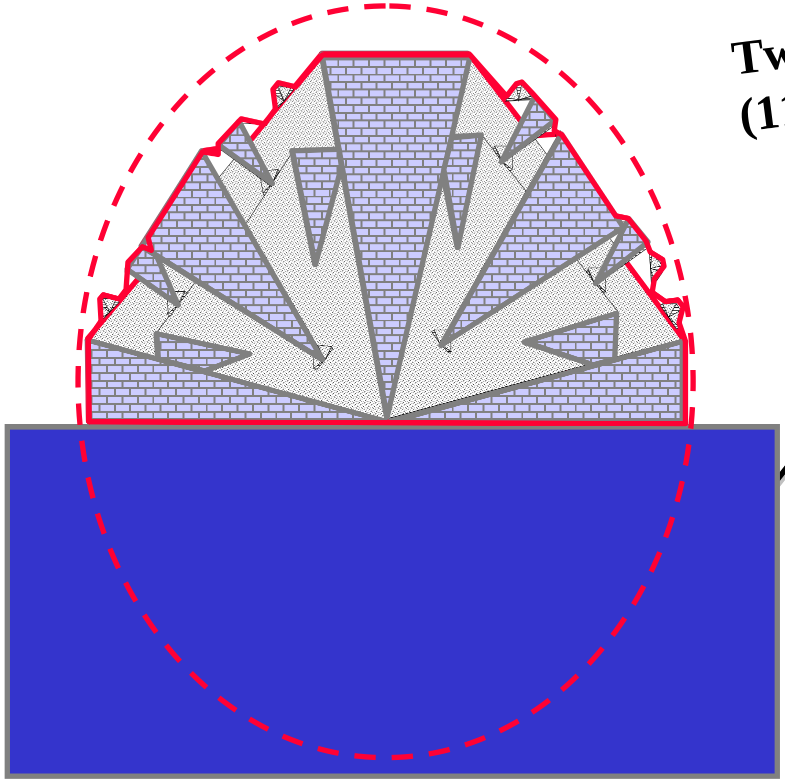
•Ts low ➔slow diffusion

•$[C_x]$ High ➔ high precurssor flux

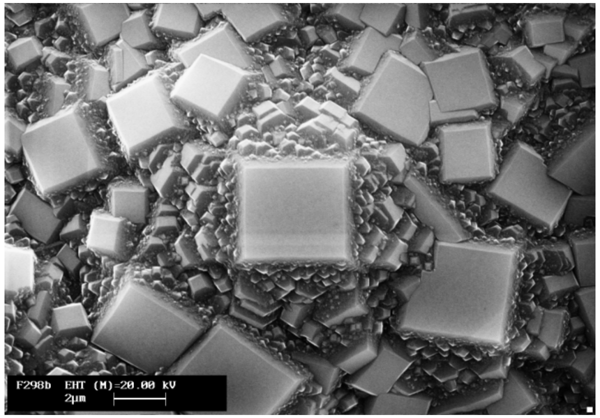


High microscopic roughness

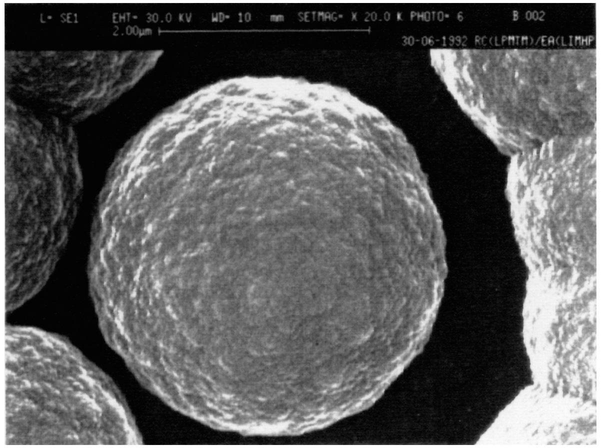
Diamond growth – mesoscale
Secondary Nucleation and twining Growth



Twining rate
(111) >> (100)
selective



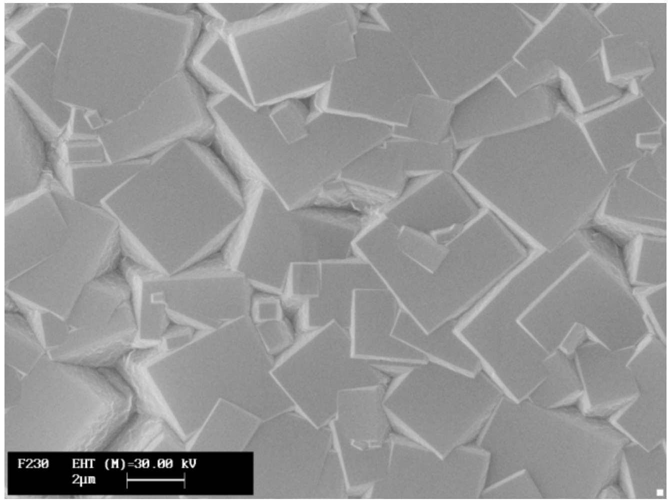
Twining rate
(111) ≈ (100)
non selective



F. Silva et al. Diam Rel. Mater.

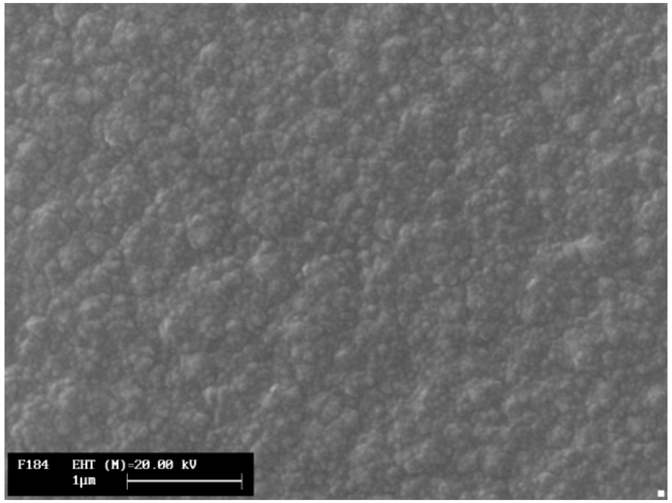
Consequence on the film morphology and texture

- selective secondary nucleation :
  - Stable (100) faces
  - unstable (111) faces



ν *«isotropic» secondary nucleation :*

  - *unstable (100) faces*
  - *Unstable (111) faces*



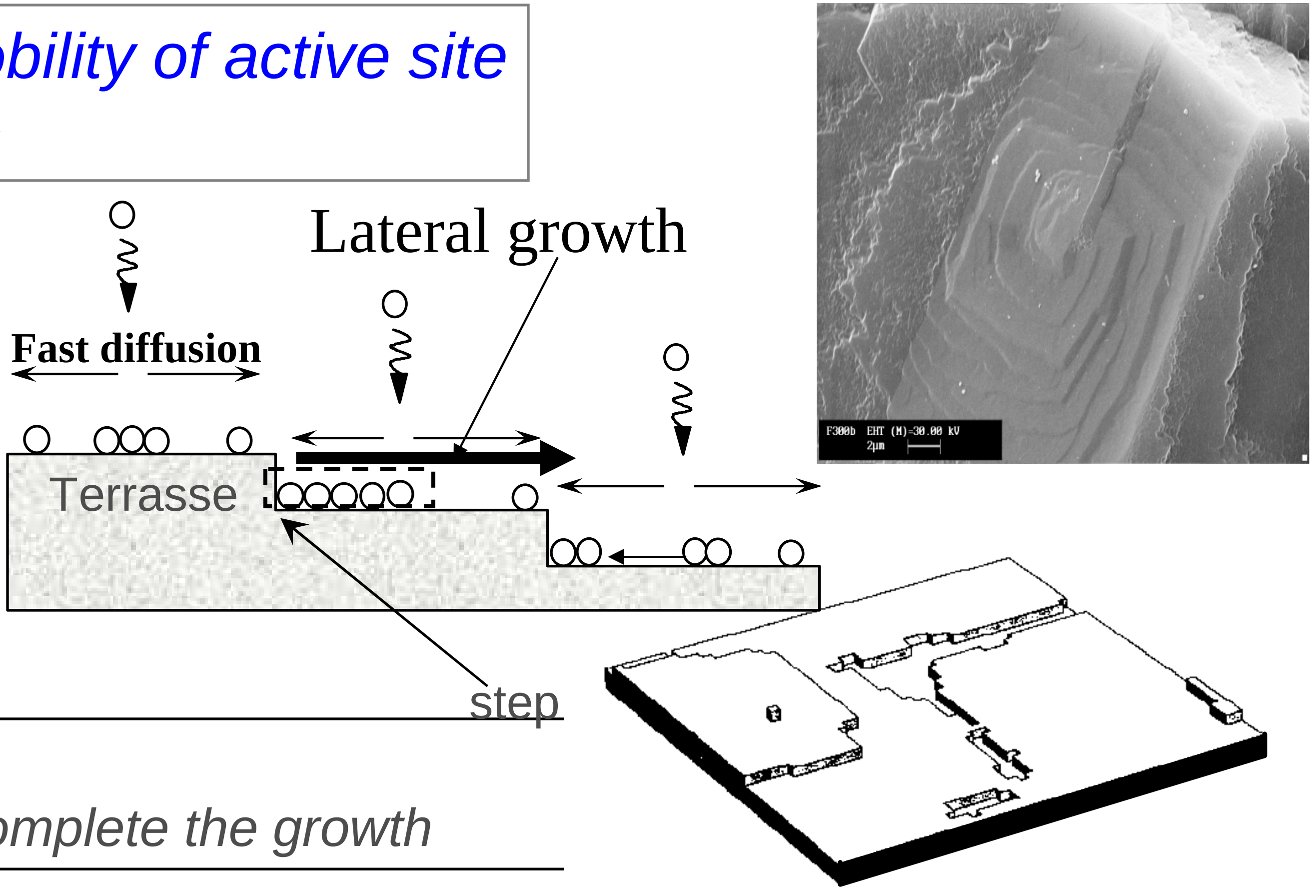
Diamond growth –mesoscale - How to interpret our observation
Step flow growth

- Low flux of the precursor species

Diffusion length > terrasses length :

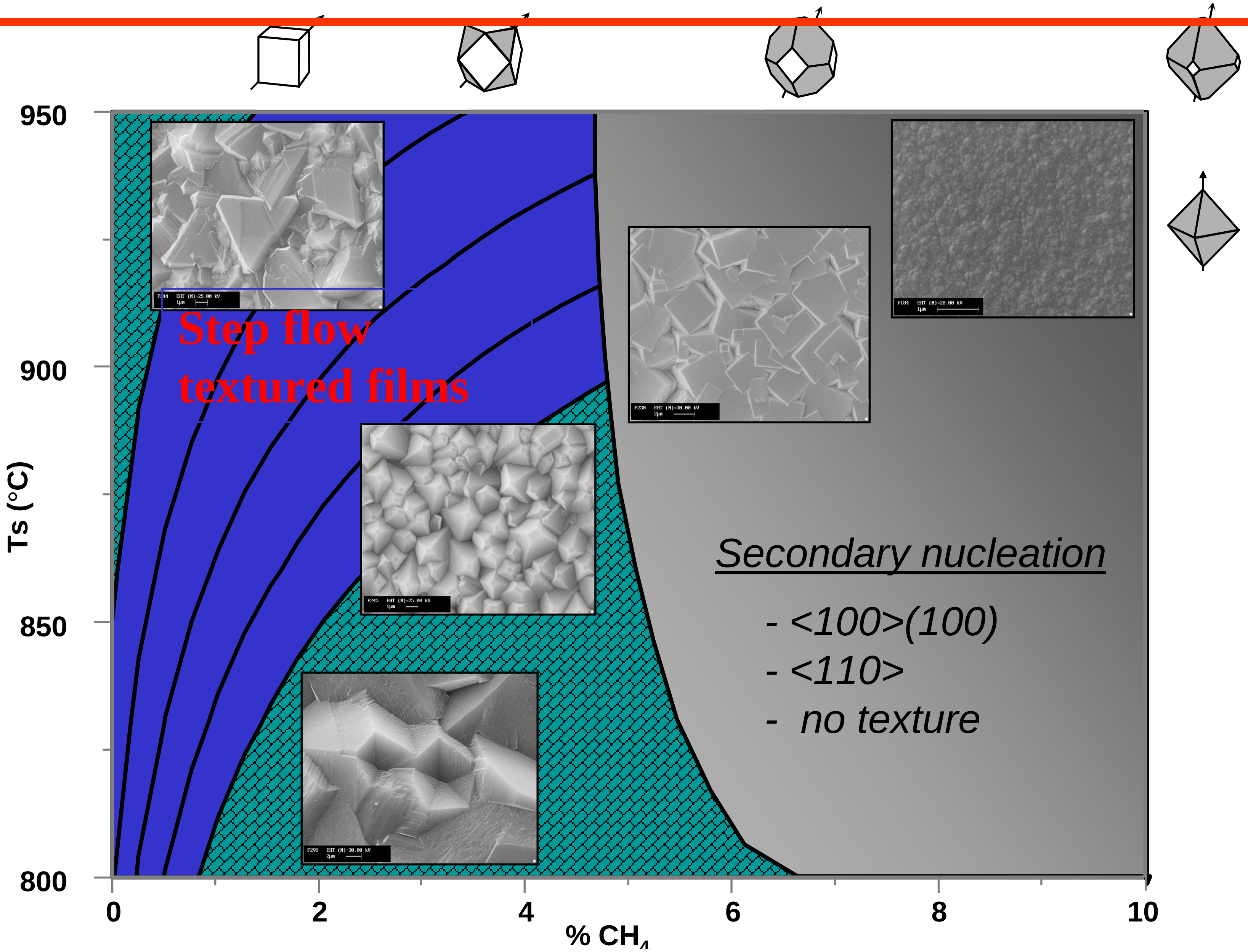
Step Flow Growth

- *Ts high ➔ high mobility of active site*
- *$[CH_3]$ low vs [H] ➔*



Smooth films
Need 2D nucleation to complete the growth

Microstructures control



Step flow textured films

Secondary nucleation

- *<100>(100)*
- *<110>*
- *no texture*

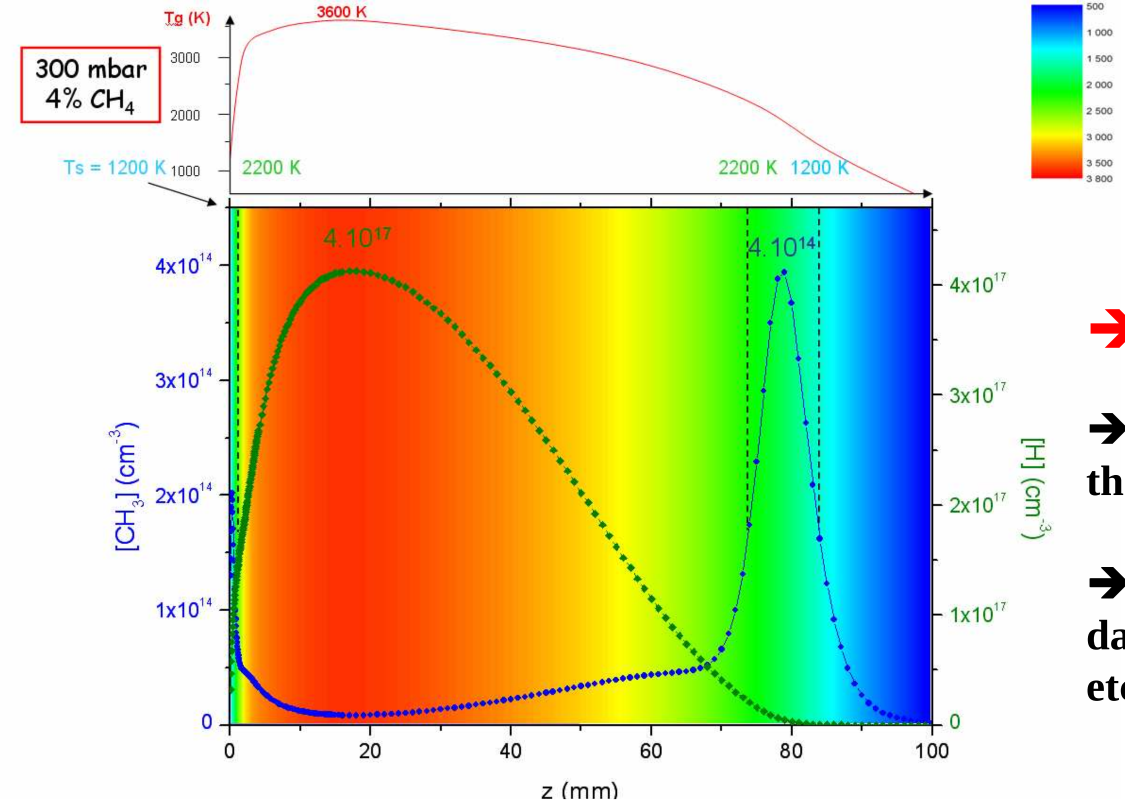
A synthetic view of diamond deposition

For Diamond deposition , Plasma = generator of H & « CH_3 »

In principle : plasma surface interaction governed by : $F_H|_{s}$, $F_{CH3}|_s$ and T_s

F_H : non-equilibrium ⇔ flexibility ⇔ possibility to monitor with process parameter

F_{CH3} = partial equilibrium ⇔ $f(F_H|_s, T_s, C/H)$



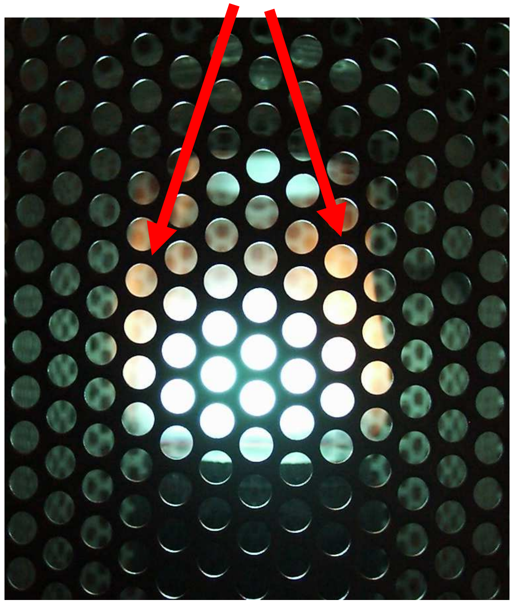
➔key role of H-atom & T_s

➔Monitor the plasma composition at the substrate

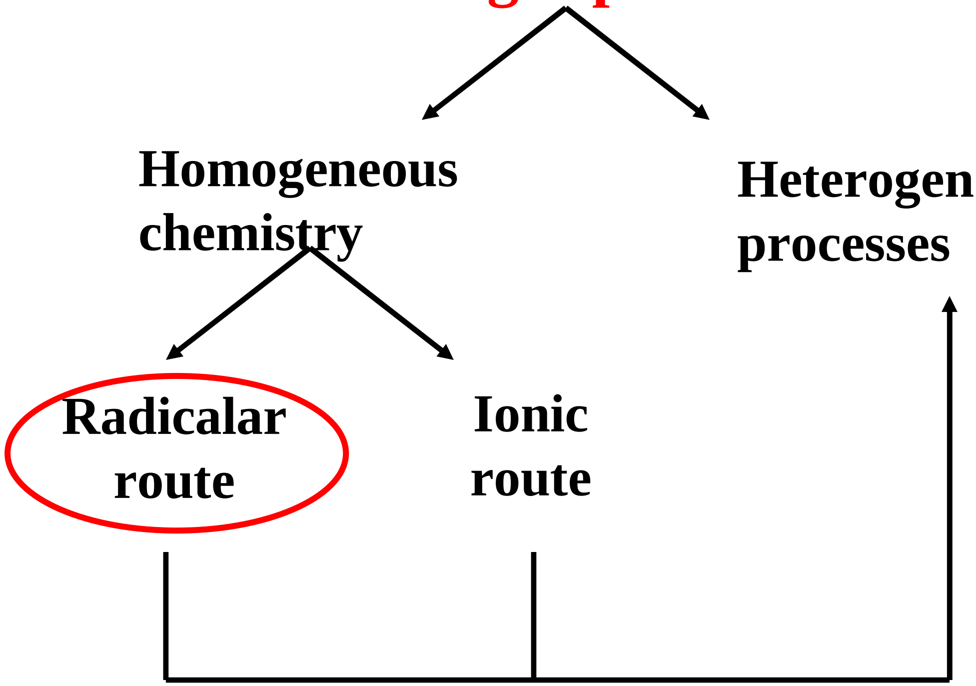
➔ affects the surface stability : dangling bonds, surface reconstruction, etc.

From H_2/CH_4 to $H_2/Ar/CH_4$

From PCD to NCD


Redish soot particles

Molecular and particle growth in gas phase



Homogeneous chemistry

Heterogeneous processes

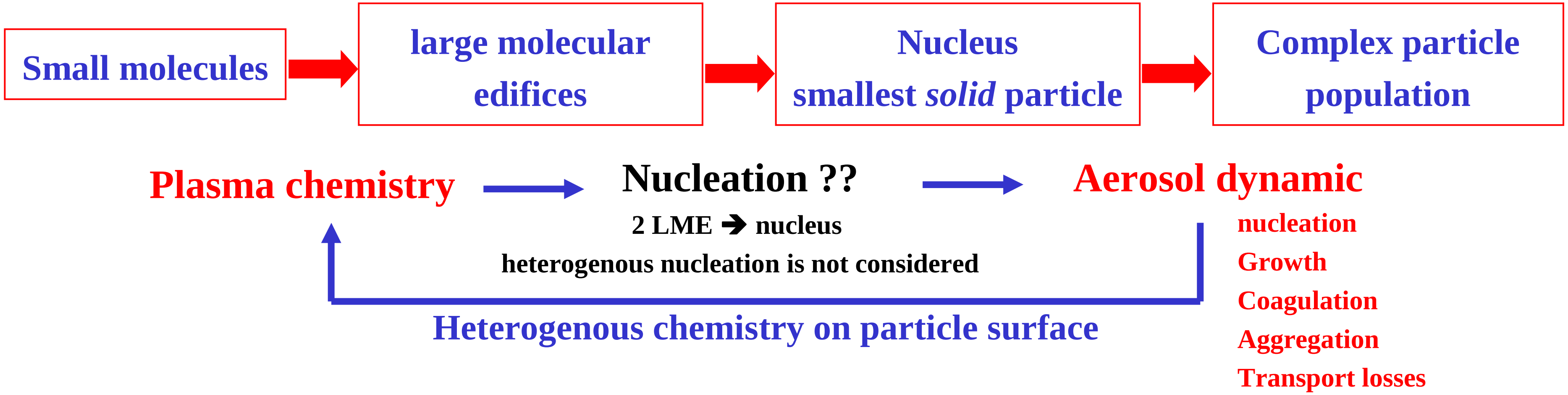
Radicalar route

Ionic route

Implication
on the growth ?
and change in the film microstructure ?

Understanding the soot formation
A modeling approach : quasi-homogenous plasma assumption

Modeling objective : estimate the gas and electron temperatures, species densities, particle size distribution (or its moments) in the uniform plasma bulk



Small molecules → **large molecular edifices** → **Nucleus smallest *solid* particle** → **Complex particle population**

Plasma chemistry → **Nucleation ??** → **Aerosol dynamic**

2 LME ➔ nucleus

heterogenous nucleation is not considered

nucleation
Growth
Coagulation
Aggregation
Transport losses

Heterogenous chemistry on particle surface

Solutions of the coupled set

- < ε_e > eq.
- Total energy eq.
- Species eq.
- Aerosol dynamic eq.

T_g, composition, < ε_e >, particle-size distribution (or its moments)

2C-model (1)

Based on the kinetic models developed for H_2/CH_4 discharges(1,2):

- **38 species (with e^-)**
  - **Neutral and charged hydrogen compounds:**

    H_2, H, H(n=2), H(n=3), H^+, H_2^+ and H_3^+
  - **Hydrocarbon molecules up to 2 C-atoms and their corresponding ions:**

    C_xH_y (x = 1-2, y = 0-6), $^1CH_2$, C^+, $CH_{3\text{-}5}^+$, C_2^+, $C_2H_{1\text{-}6}^+$
  - **Argon based compounds:**

    Ar, Ar^*, Ar^+, ArH^+ and ArH^{+*}

- **147 chemical reaction mechanism describing**
  - **the chemistry of pure hydrogen discharge**
  - **the thermal hydrocracking of H_2/CH_4 mixture**
  - **the chemistry of hydrocarbon ions**
  - **the reactions due to the presence of argon**

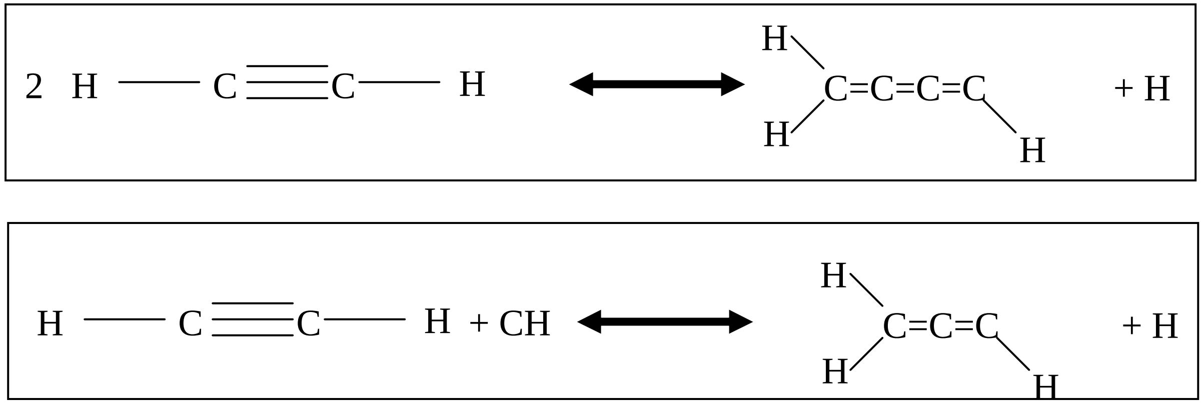
(1) *Hassouni et al., Plasma Chem. Plasma. Proces*
(1998)

(2) *Hassouni et al., Plasma Sources Sci. Techn*
(1998)

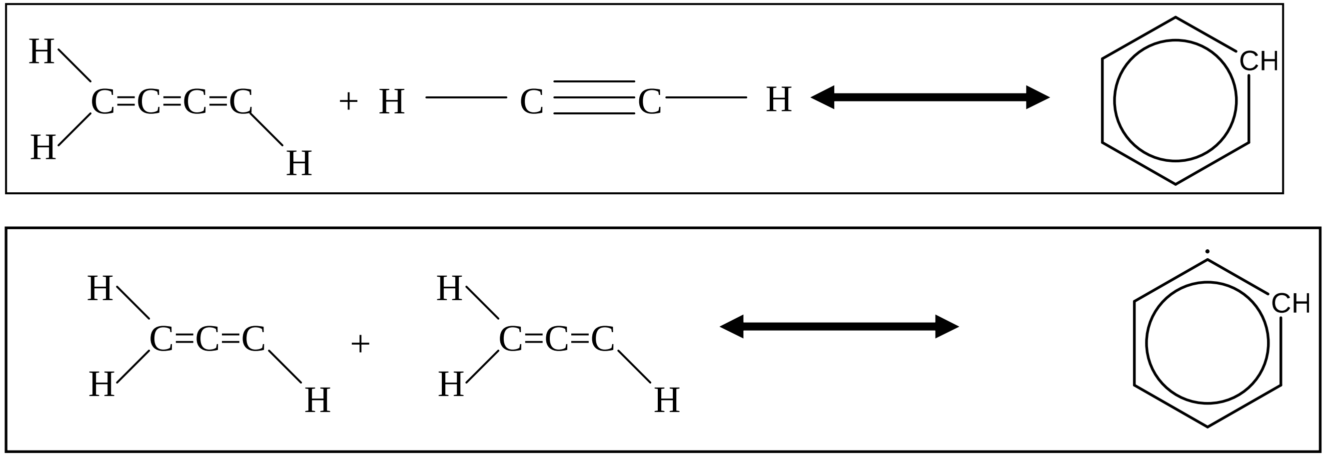
A4/A9 models (1)

Radicalar growth of PAH and nucleation mechanism

- **Mechanism of Poly-Aromatic Hydrocarbons (PAHs) formation**⁽¹⁾



Linearization



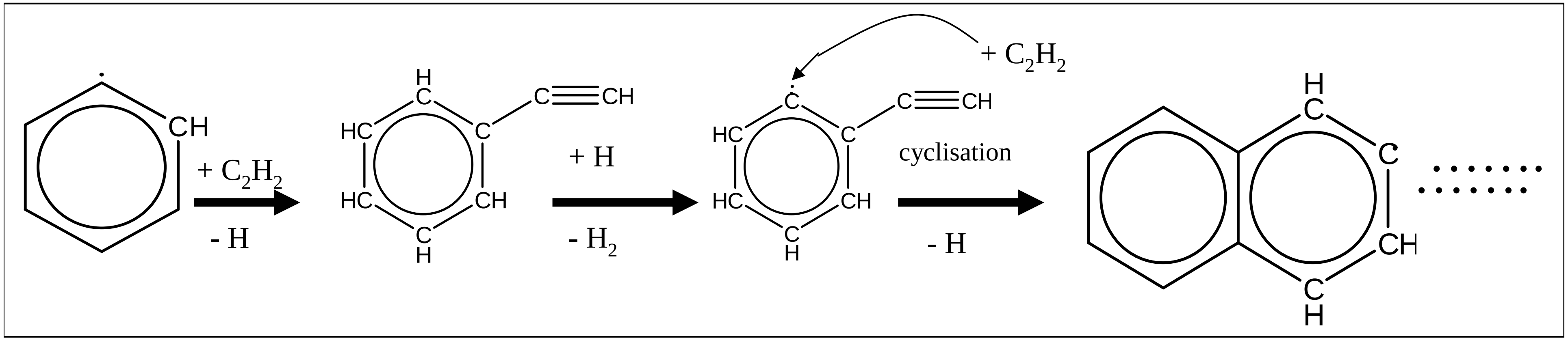
Cyclization

(1) *Wang et Frenklach., Comb. Flame (1997)*

A4/A9 models (2)

Radicalar growth of PAH and nucleation mechanism

Hydrogen Abstraction Carbon Addition (HACA)



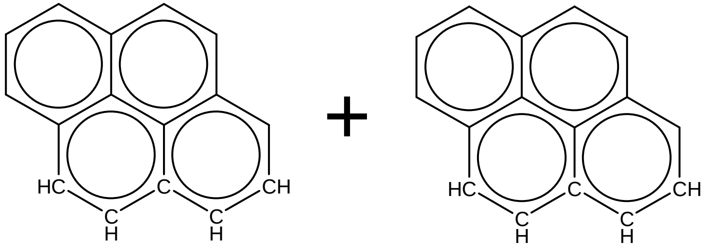
[(1)] *Wang et Frenklach., Comb. Flame (1997)*

A9/A4 models (3)
Nucleation mechanism

- Nucleation of soot particles

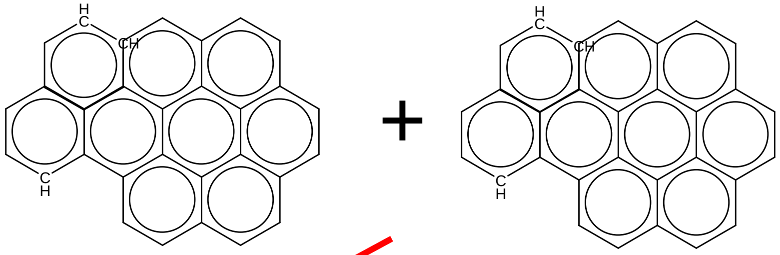
2 models were considered

Condensation of 2 pyrene molecules



A4 **A4**

Condensation of 2 dibenzo-coronene molecules

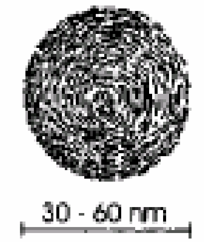


A9 **A9**

A4-model

Soot nucleus

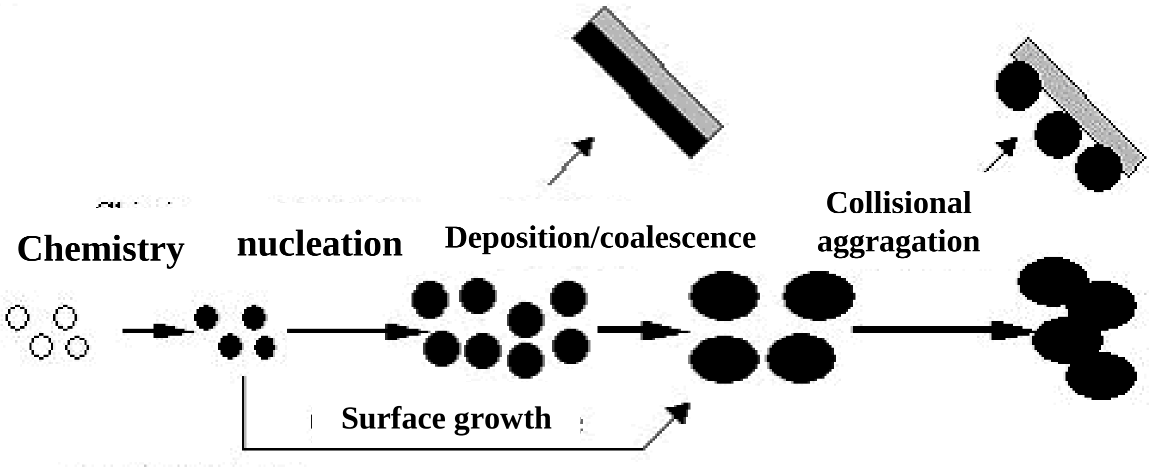
A9-model



Soot particle

See the work of Frenklach group

The aerosol dynamic governing equations



$$\frac{dN_i}{dt} = \tilde{R}_i + \tilde{G}_i + \tilde{W}_i + \tilde{T}_i$$

N_i : density of particles with a size i

R = nucleation rate (estimated from the chemical kinetics model)

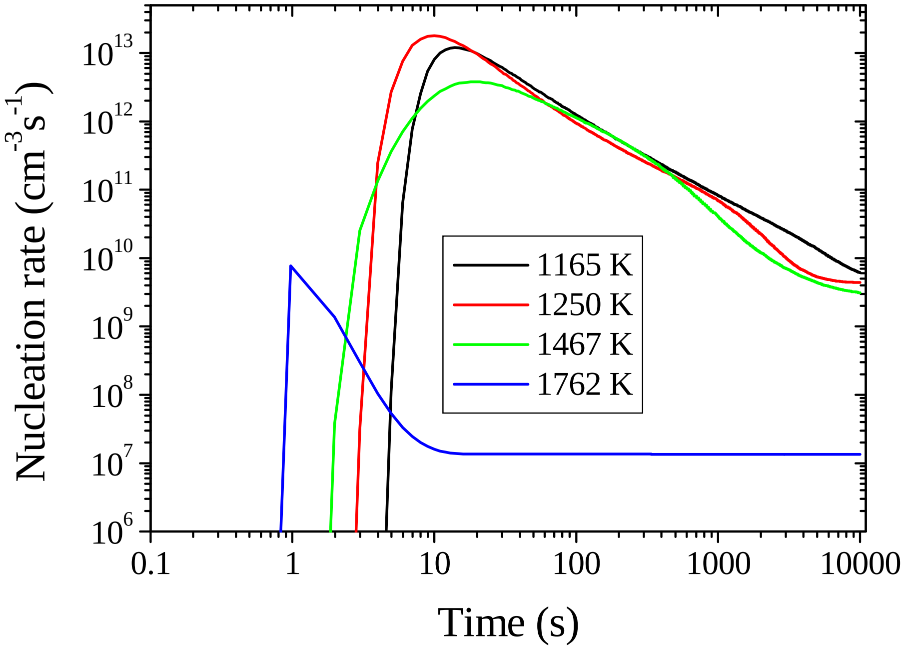
G = <u>coagulation</u> rate (2 particles ➔ larger particles)

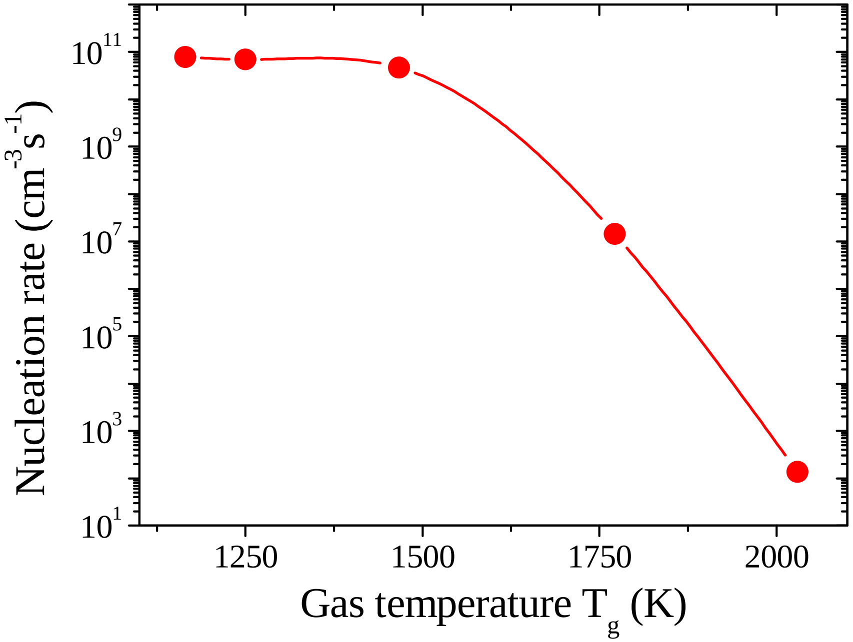
W = growth rate (surface growth - hetergenous chemistry)

T = particle losses due to transport : diffusion, thermophoresis, drag, etc..

Radical mechanisms models: A4-model (8)

✓ Nucleation of soot particles





➯ Time-scale for soot formation ≈ 1-10 s

➯ High nucleation rate below 1500 K

➯ Strong decrease for higher T_g

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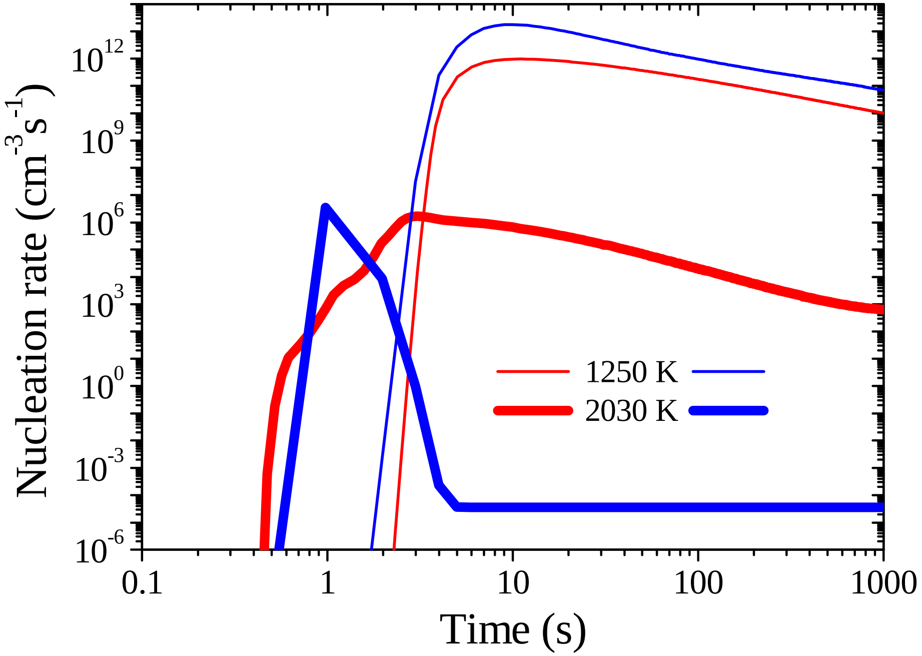
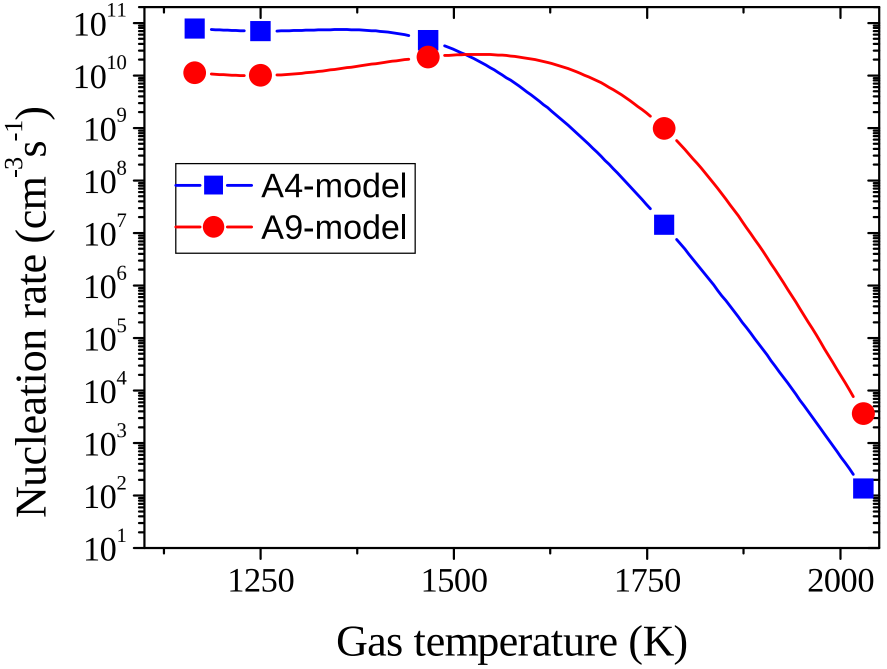
Radical mechanisms models: A9-model (13)

✓ Nucleation of soot particles

A4-model **A9-model**





➪ Except at high temperature the trends are essentially the same

➪ A9 model yields a somewhat wider temperature domain for nucleation

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Self consistent modeling of chemistry and aerosol dynamic

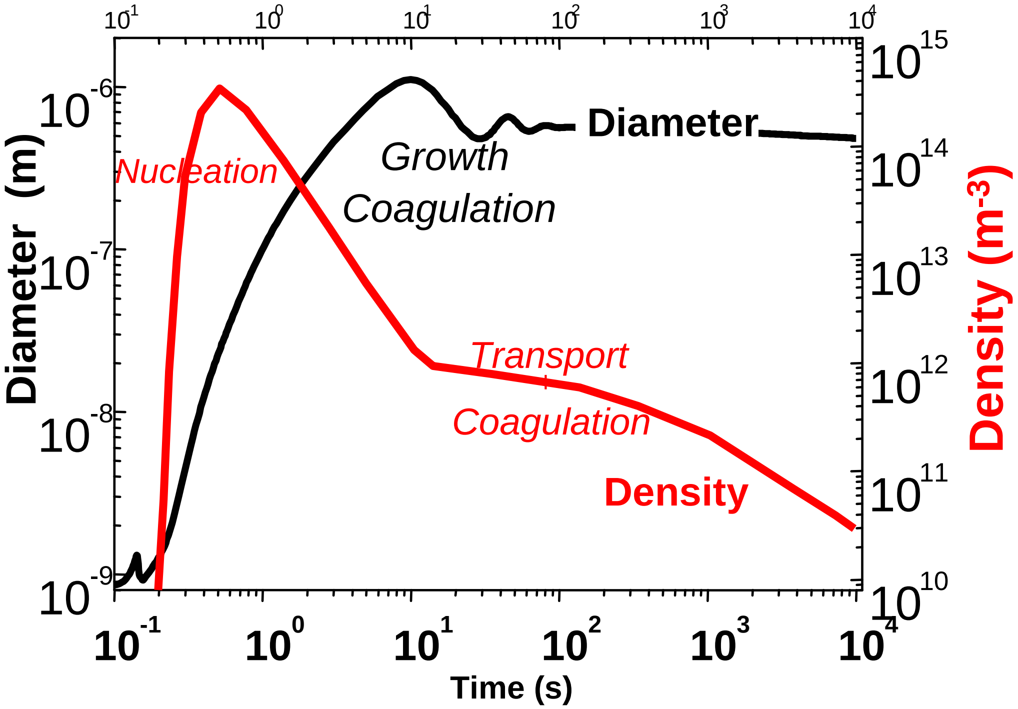
Feed-back of soot particles on the plasma chemistry takes place through heterogeneous condenstation reactions which depends on the 2/3 order moment (soot surface per unit volume).

$CH_4/H_2/Ar$ (1/2/97 %),

200 mbar

T_g = 1450 °C

condensation coefficient on soot = 10^{-3}



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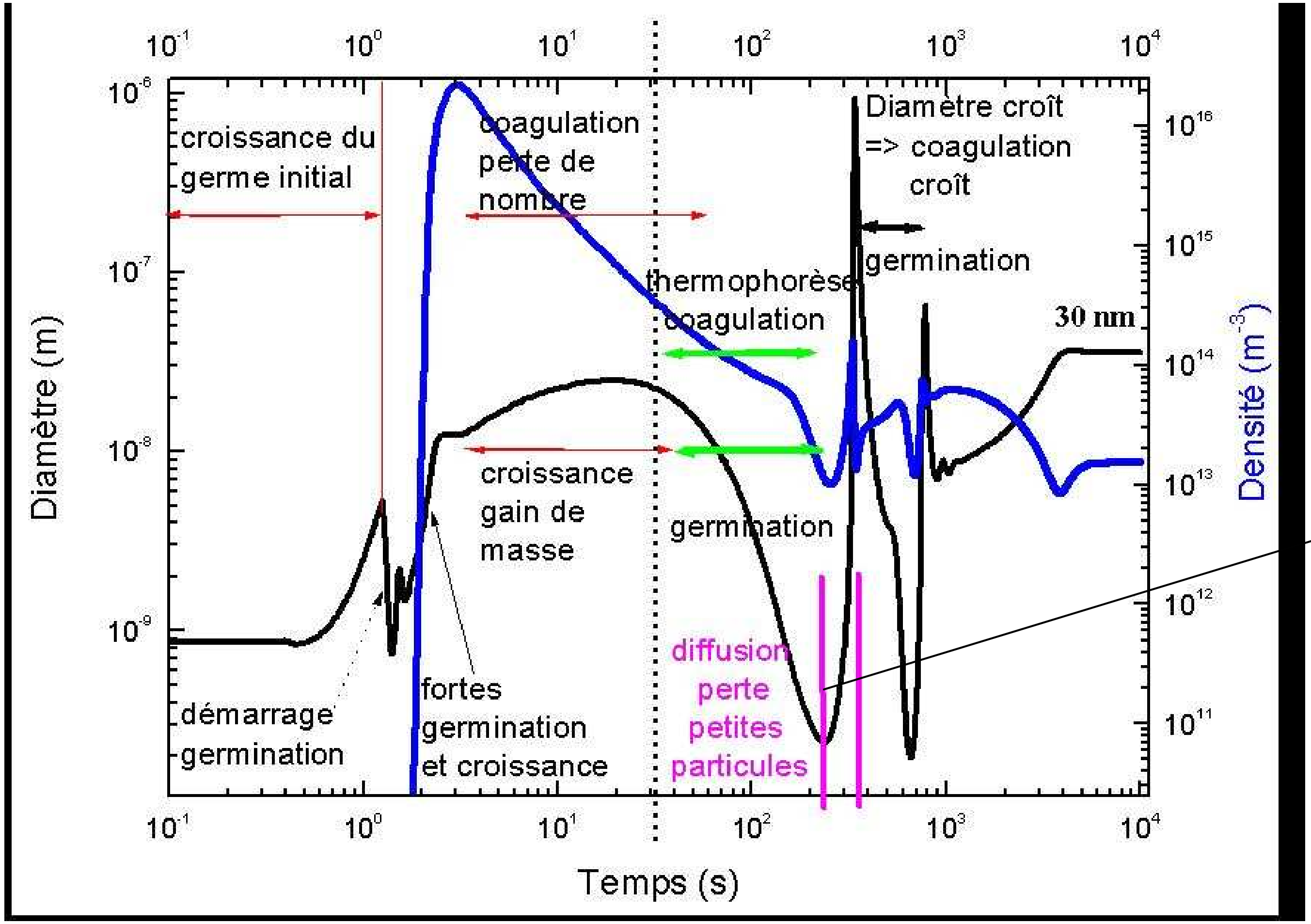
Self consistent modeling of chemistry and aerosol dynamic



Very high particle fluxes on the substrate

Significant nucleation (10^7 cm^{-3}) in the cold region of the plasma

Up to H/C = 16 !!!! ➔ implication on film growth ????

Negative ions driven molecular and particle growth in plasma :

Trapped in the discharge

- ➔very long residence time
- ➔No interaction with « surfaces »

Very long residence time

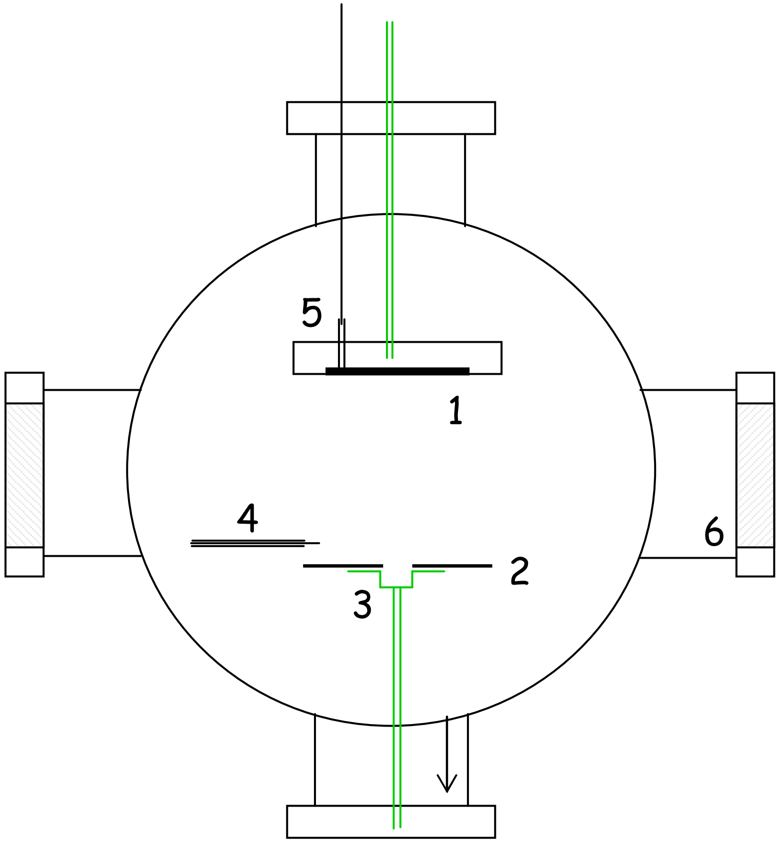
- ➔molecular growth
- ➔particule formation
- ➔Significant impact of the plasma dynamic

Two examples :

- •Carbon particles from DC sputtering of graphite
- •Hydrogenated silicon clusters SiH_4/H_2 RF discharges

Particle generation through plasma surface interaction : the role of negative ions

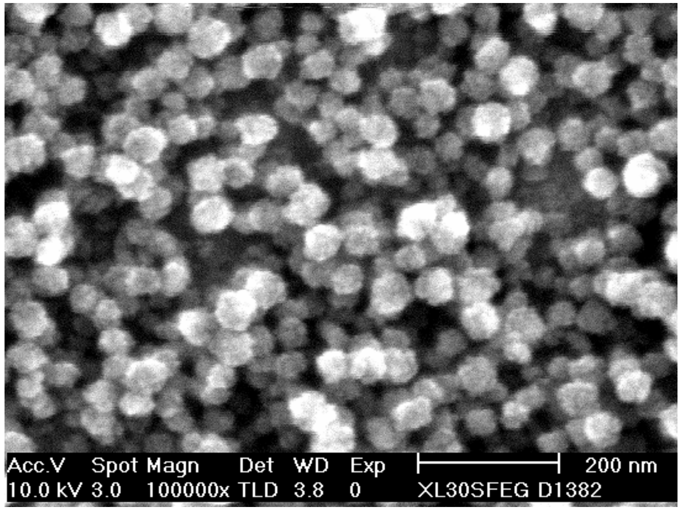
- DC discharge in Argon
- Inter-electrode distance from 4 to 14 cm
- Bias V_d ~ - 600 V
- Discharge current = 80 mA
- $N_e = N_i = 10^{10}$ cm^{-3} in the negative glow
- T_e ~ 3 eV
- Pressure = 0.1 - 1mbar (typically 0.6 mbar)
- The only carbon source is the graphite cathode
- Discharge duration < 20 min



1 : Graphite cathode
2 : Anode
3 : Dust collector
4 : Langmuir probe
5 : Thermocouple
6 : Optical window

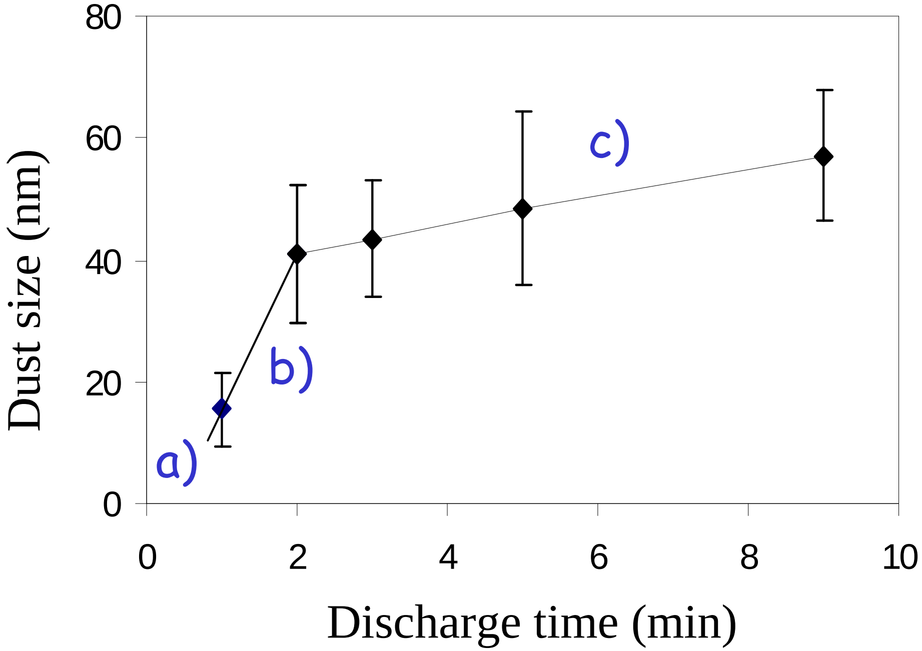
Carbon dust in the PIIM reactor

SEM micrograph



Quasi-spherical particles
Around 44 nm in diameter after 3 min of discharge

Experimental growth rate



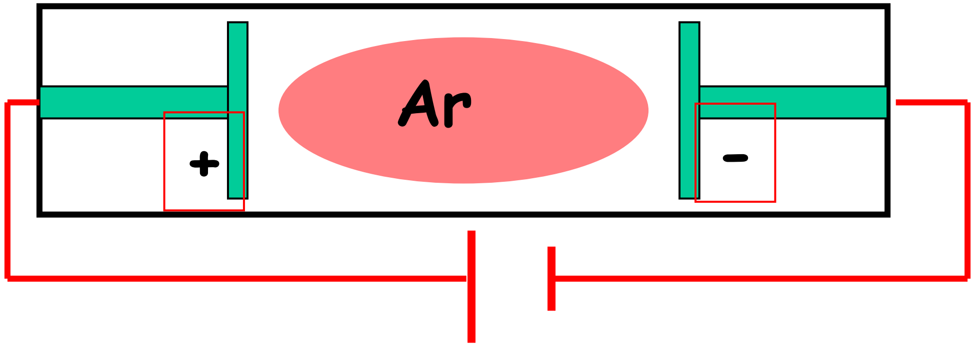
a) Growth of molecule precursors (neutral and ions) → formation of primary particles

b) Growth rate: 23 nm/min : agglomeration of primary particles

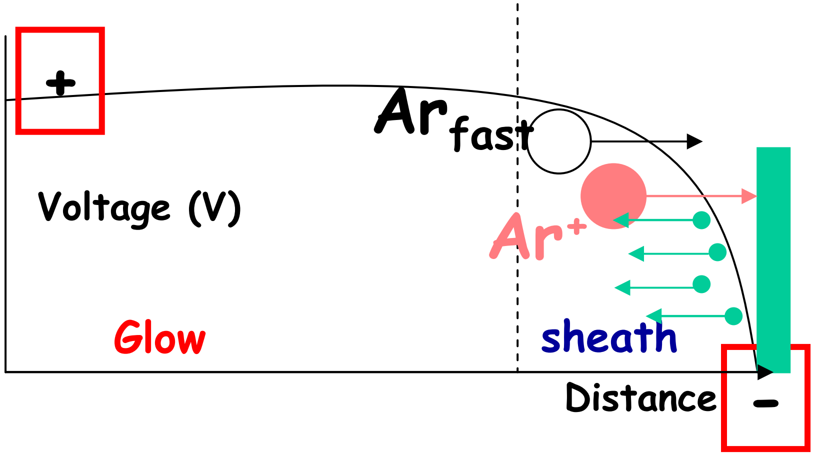
c) Growth rate: 2,4 nm/min : growth by deposition

Understand this particle formation :Model of nucleation, growth and transport of dust in Ar DC discharges

PIIM device



Voltage: - 600 V
Inter-electrode distance: 14 cm
Electrode diameter: 5 cm
Current: 8×10^{-2} A

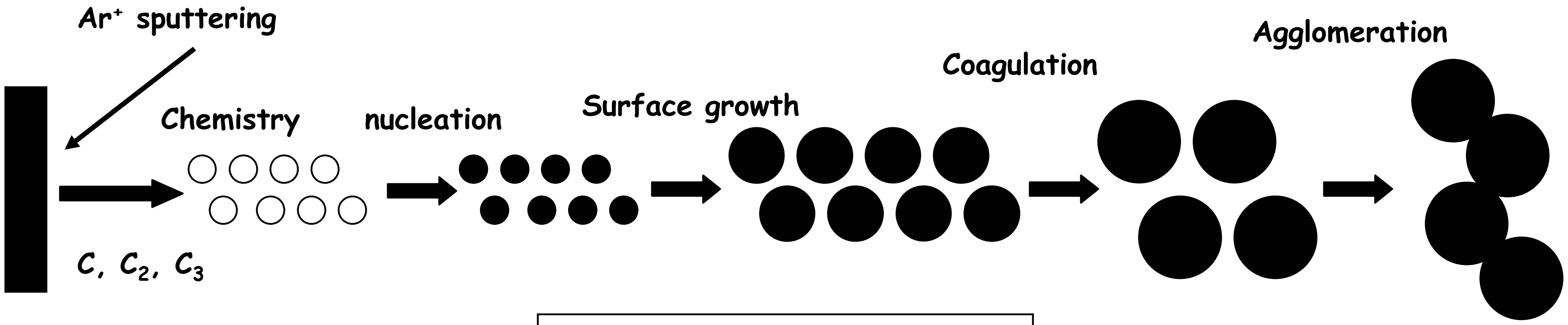


$Ar_{slow} + Ar^{+} \rightarrow Ar^{+} + Ar_{fast}$

Dusts are produced by the sputtering of the graphite cathode:

- Argon ions accelerated in the sheath
- Fast neutrals resulting from charge transfer

Dust formation : speculated mechanism



$$\boxed{\frac{dN_i}{dt} = \tilde{R}_i + \tilde{G}_i + \tilde{W}_i + \tilde{T}_i}$$

N_i = density of particles with a size i
R = nucleation rate (estimated from the chemical kinetics model)
G = coagulation/agglomeration rate (two particles ➔ larger particles)
W = growth rate (surface growth - heterogeneous chemistry)
T = particle losses due to transport : diffusion, thermophoresis, drag, ...

Model of nucleation, growth and transport of dust in DC discharges ignited in Ar (2)

- ✓ Estimation of discharge main characteristics: *flux and ion energy distribution or ion average energy on the cathode*
- ✓ Extraction of C_1, C_2 et C_3
- ✓ Formation of $C_{n=1,nl}$ clusters, where n_l is arbitrary chosen (n_l=30 or 60)
- ✓ Nucleation of carbon dusts from clusters: *Assumption of 'Largest Molecular Edifice'*
- ✓ Growth, transport and wall losses of dusts
- ✓ Dust charging
- ✓ Size distribution of dusts

Molecular growth modelling of carbon clusters and dusts

Molecular growth

$$\frac{\partial n_{i,z}}{\partial t} = -\vec{\nabla}\left(-D_i\vec{\nabla}n_i + \mu_{i,z}nz\vec{E}\right) + \boxed{W_i}$$

Diffusion Mobility

Production rate of the C_i cluster

clusters

Nucleation

$$\frac{\partial n_{n_l,z}}{\partial t} = W_{n_l}(n_l) = N$$

$n_{i,z}$ = density of the cluster C_i of charge z

Dust Transport

$$\frac{\partial n}{\partial t} = -\vec{\nabla}\left(-D.\vec{\nabla}n + \mu.n.\overline{z}.\vec{E}\right) + N - C$$

$$\frac{\partial \rho}{\partial t} = -\vec{\nabla}\left(\left(-D.\vec{\nabla}n + \mu.n.\overline{z}.\vec{E}\right)\overline{M}\right) + N + A$$

N = nucleation
C = coagulation
A = condensation

⇒ Determination of the average diamater d_p

Carbon cluster growth reactions**

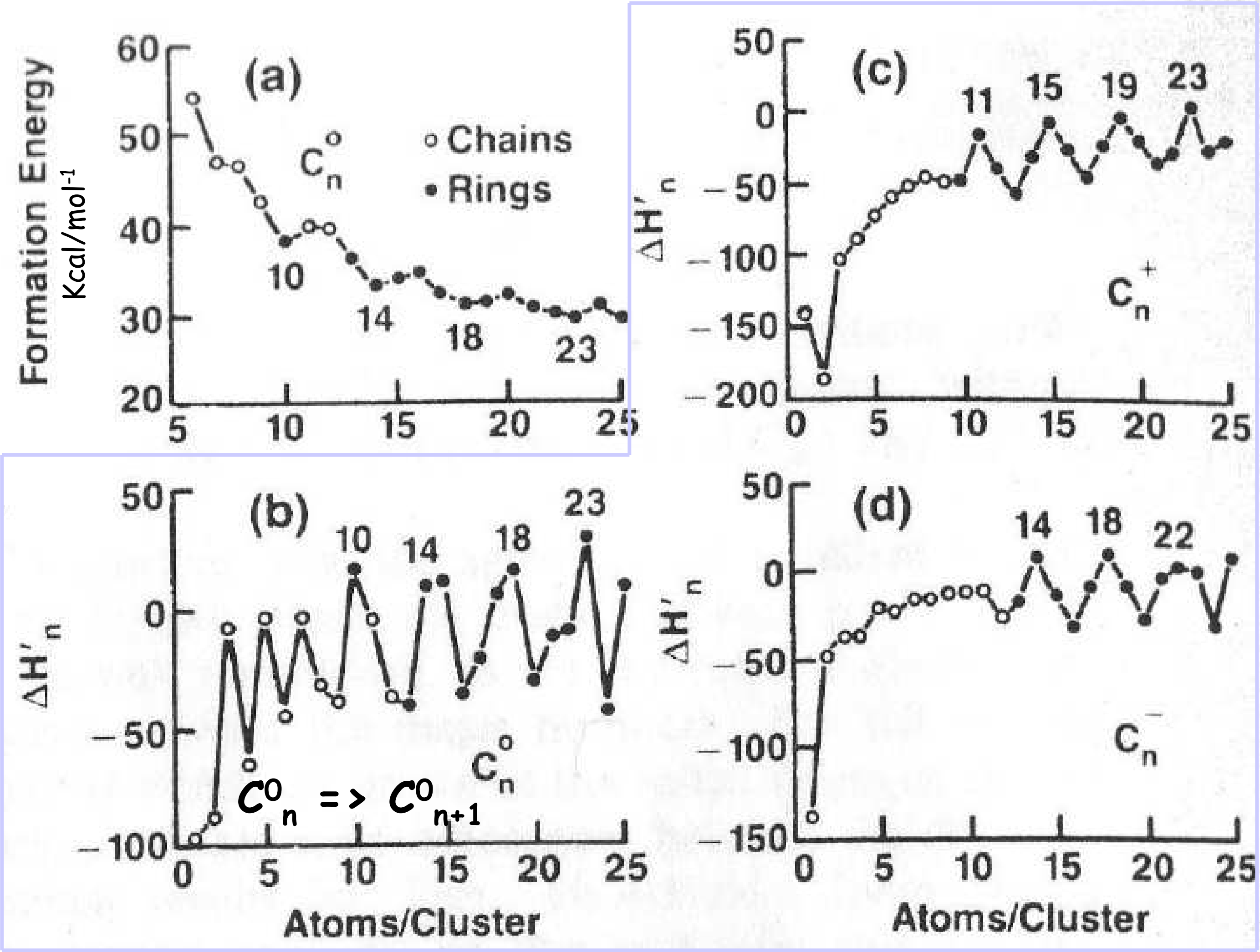
Bernholc & Schweigert models (classical models) (**):

- Growth = one single process ($C_n + C_x \rightarrow C_{n+x}$), but take into account the stability of the C_n clusters

- First version of the model took into account neutral clusters

- Molecular growth of clusters
  - Rates computed according to formation enthalpies
  - Clusters have configurational isomers (chains, rings, multi-cycles) distinguished by cyclization entropy (20 kcal/mol/cycle)
  - Extrapolation for unknown values according to cluster periodicities

Formation enthalpies



Formation enthalpies

$$k_{ij} = \alpha R_{ij}^3 e^{-\gamma \frac{\left(\Delta G'_i + \Delta G'_j\right)}{kT}}$$

$$\Delta G'_i = n\left(\Delta G_{i+1} - \Delta G_i\right) = n\left(\Delta H_{i+1} - \Delta H_i\right) - nT\left(\Delta S_{i+1} - \Delta S_i\right)$$

Molecular growth modelling of neutral carbon clusters and dusts

➔Low pressure discharge : p=10-100 Pa

➔Diffusion characteristic time =1-10 ms very short as compared to the growth chemistry ➔ no possibility for growth of neutral

➔ Need for species with higher residence time :

Negative clusters

And

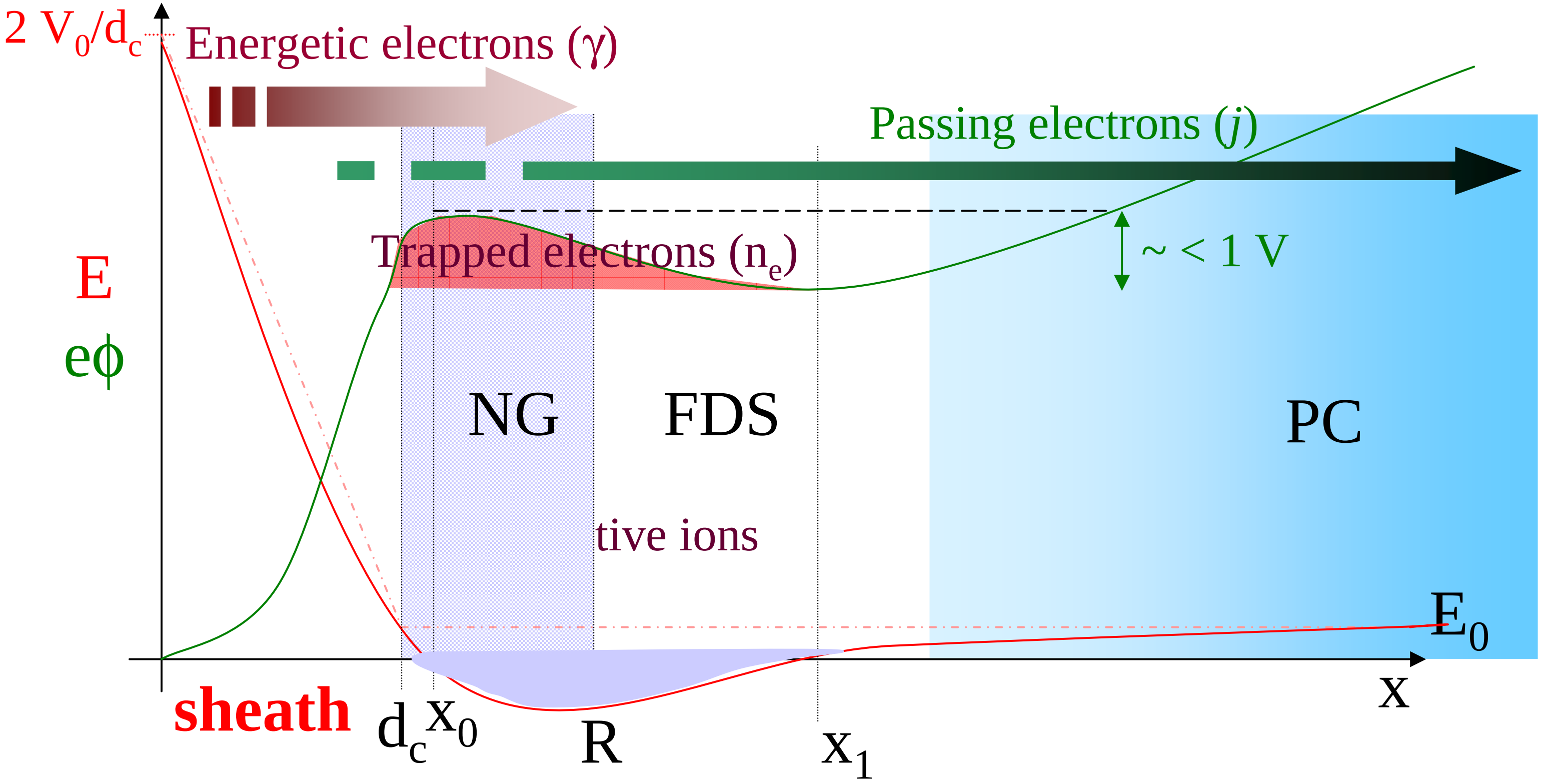
Trapping electric field configuration

➔ Back to some basic DC discharge physics

PIIM

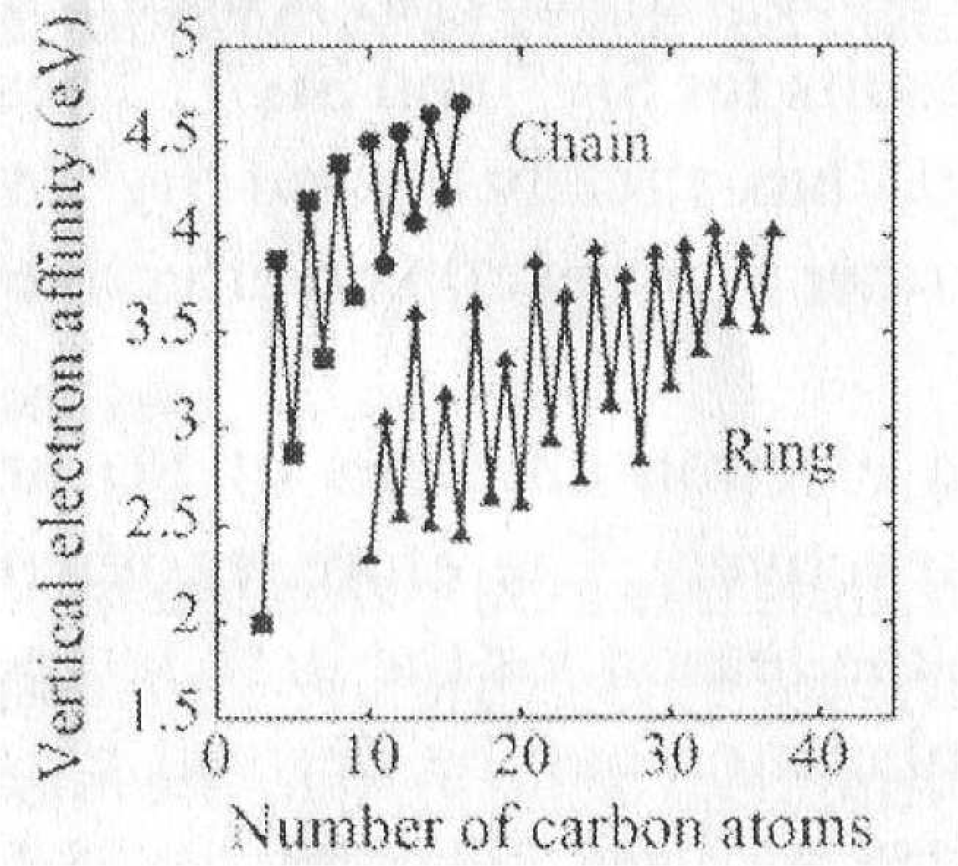
Electric field reversal and molecular growth of negative clusters

- Charging of dust particles **only effective if electric field is confining** !
- Where is the confining electric field ? ➔ Kolobov & Tsendin, Phys. Rev. A **46** 7837, Boeuf &PitchFord, J. Phys. D, (1994)
  - **Self-consistent electric field reversal: confinement**
  - Three electron populations: energetic, passing, trapped



NG: Negative glow / FDS: Faraday Dark Space / PC: Positive Column

Negative carbon cluster growth reactions



From Y. Achiba et al., J. Elect. Spect. Related Phen. 142, 231 (2005)

- <u>Attachment</u> $C_n + e^- \rightarrow C_n^-$
  - Rates computed according to electronic affinities
- <u>Charge exchange</u> $C_n^- + C_x \rightarrow C_n + C_x^-$
  - Electronic affinities

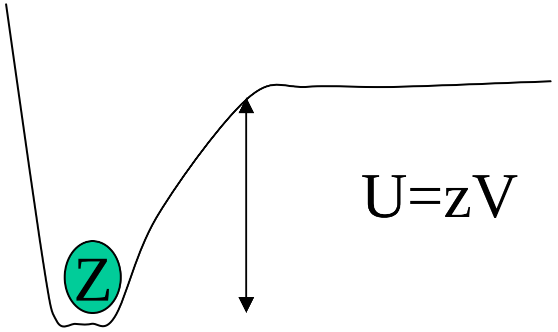
$$T_{i^- j} = \alpha R_{ij}^3 e^{-\xi - \frac{\Delta A_i + \Delta H_j}{kT}}$$

- <u>Dust agglomeration</u> (sticking)
- <u>Detachment</u> $C_n^- + e^- \rightarrow C_n + 2e^-$

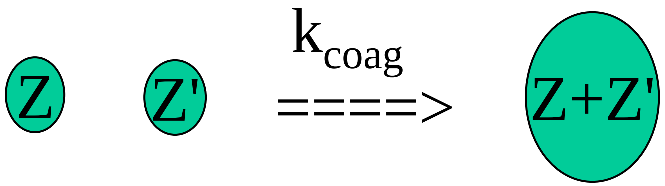
carbon particles aerosol dynamic in a DC dicharge

Particle charging is a key point :

==> Enhanced particle charging insures a significant trapping and long residence time

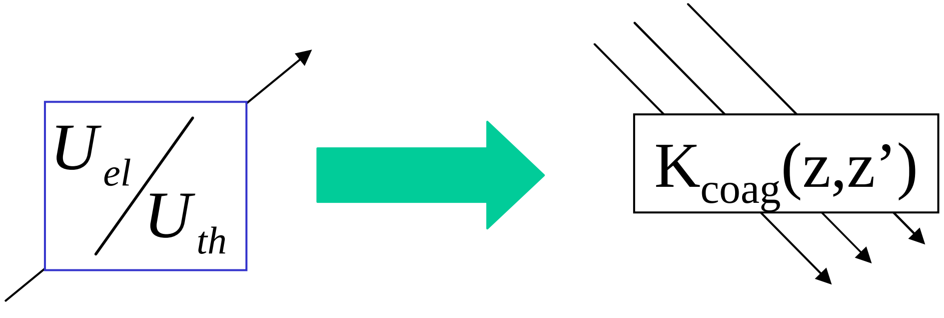


==> Enhanced particle charging prevents coagulation and growth



$$k_{coag}(z,z') = \frac{k_{coag}(0,0)}{w(z,z')}$$

$$w(z,z') = \frac{\exp\left(U_{el}/U_{th}\right) - 1}{U_{el}/U_{th}}$$



The only way to have growth ==> charge fluctuation and electron depletion

Possible because particle charging is a discrete process ➔ Dynamic fluctuation of small particles between positively and negatively charged states

➔ Coagulation takes place between two particles that has opposite instantanous charges or no charge ➔ involve small particles.

$$\tau_{coag} << \tau_{fluctuation} << \tau_{trans}$$

Transport feels the average charge

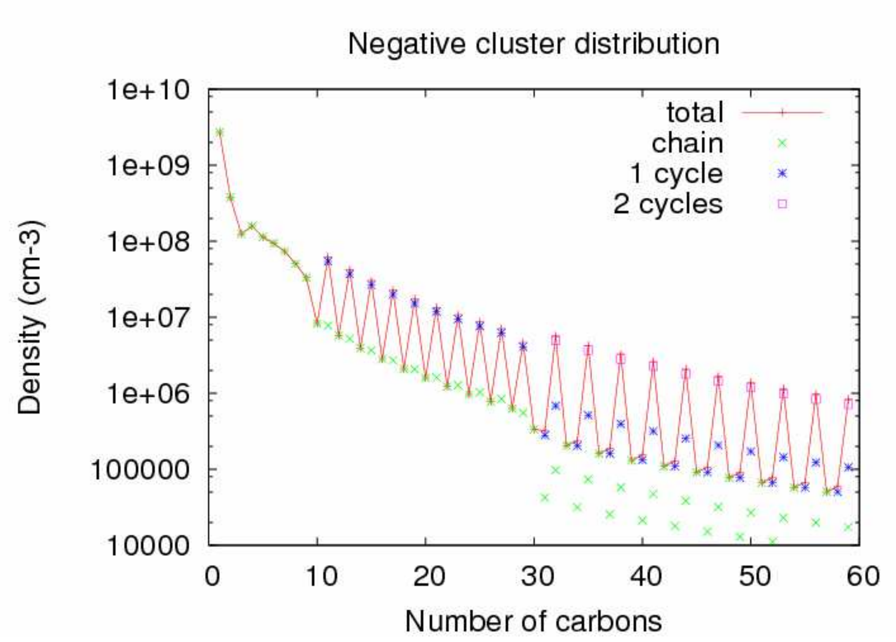
$$\frac{d\bar{q}_i}{dt} = -\frac{div(\vec{J}_i - \bar{q}_i div(\vec{F}_i)}{n_i} + \frac{wq^{+}_{coag} - \bar{q}_i w^{+}_{coag}}{n_i} + \frac{wq^{+}_{growth} - \bar{q}_i w^{+}_{growth}}{n_i} + \frac{I^{+} - I^{-}}{n_i}$$

Coagulation feels the fluctuations

Fluctuation

$$\psi(q,\bar{q}) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(q-\bar{q})^2}{2\sigma^2}\right] \quad \sigma = f\left(\frac{T_e}{T}, \frac{U_{el}}{U_{th}}\right)$$

Negative clusters

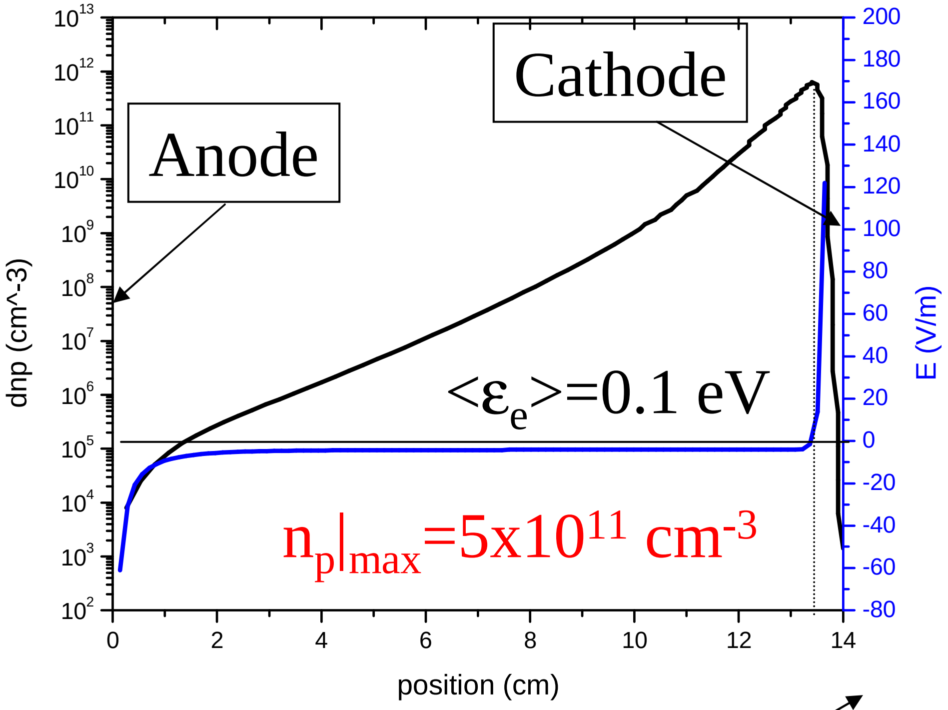


Negative clusters have significant densities

→ Growth rate is a function of the electric field profile in the discharge

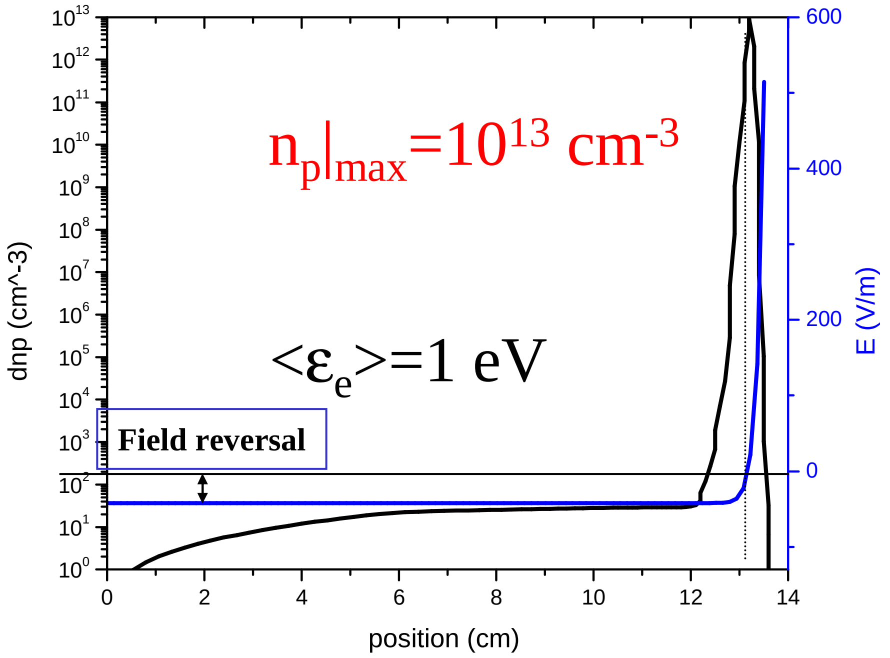
→ An accurate knowledge of the field profile is required

Dust density



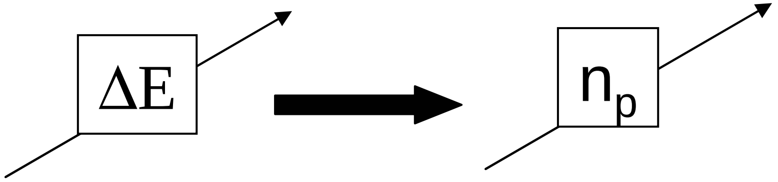
$\langle \varepsilon_e \rangle = 0.1$ eV

$n_p|_{max} = 5\text{x}10^{11}$ cm^{-3}



$n_p|_{max} = 10^{13}$ cm^{-3}

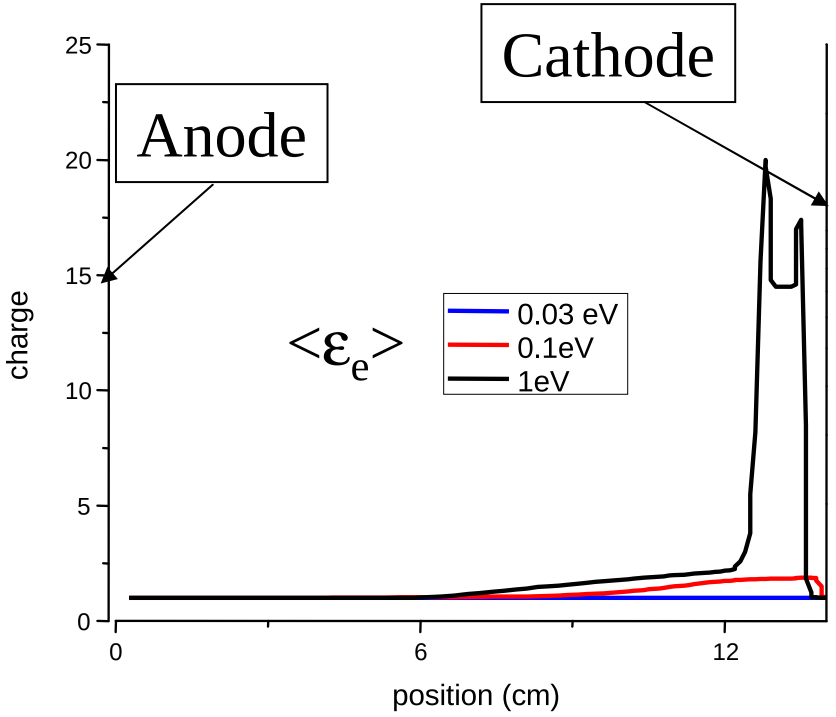
$\langle \varepsilon_e \rangle = 1$ eV

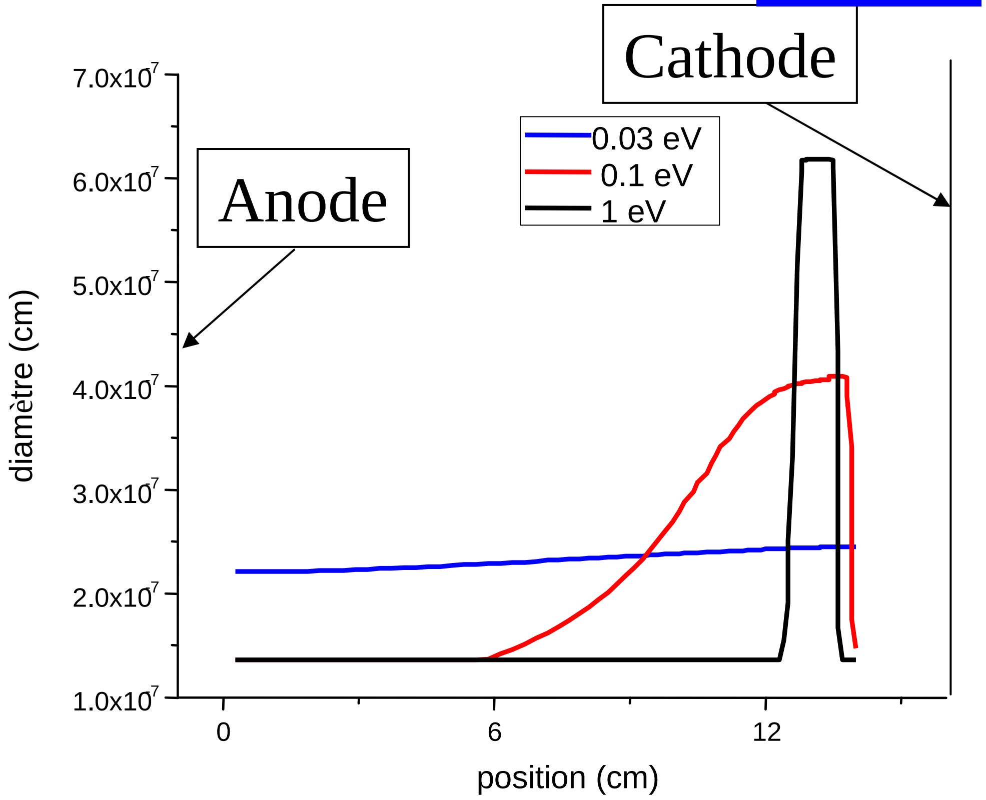


Electric field reversal <=> electron average energy in the NG

$$\Delta E \cong \langle \varepsilon_e \rangle$$

Dust average charge and diameter





It is indeed possible to explain particle formation through negative ion driven molecular growth

➔ Discharge dynamic (field reversal) and sputtering kinetics are key-points

Pbs : we need better description of the growth kinetics : Model ➔ 1 hour for dust formation (instead of few minutes)

Take into account the size and charge distributions

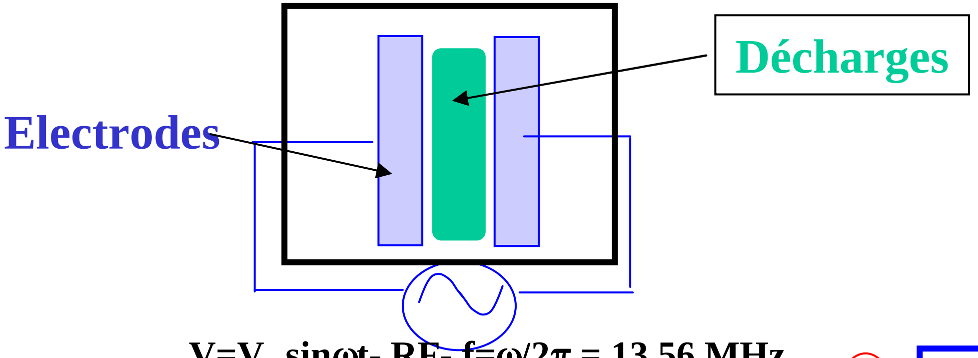
3- Hydrogenated silicon cluster growth in RF diode discharges

Coupling between plasma dynamic ➔ small ions density and energy

And

molecular dynamic to predict the growth of hydrogenated silicon cluster

Cas où l'hypothèse de localité est valable et que les électrons peuvent être traités dans le cadre du modèle continu



$V=V_0 \sin\omega t$- RF- $f=\omega/2\pi$ = 13.56 MHz

Ar/O_2-p=1 torr, T_g=300 K,
Puissance =0.1-1 W

$\lambda_{Debye} \approx 1$ cm $\approx d_{syst}$

① On tient compte de la séparation de charge (possibilité de régions non neutres)

② Pas d'effet de longueur d'onde : Hypothèse électrostatique

③ Hypothèse : diffusion-dérive

$\omega_{p\text{-}i} \ll \omega \ll \omega_{p\text{-}e}$

- OK pour les électrons
- Non pour les ions => EQM pour les ions

On contourne la difficulté en utilisant un champ électrique effectif vu par chaque ion.

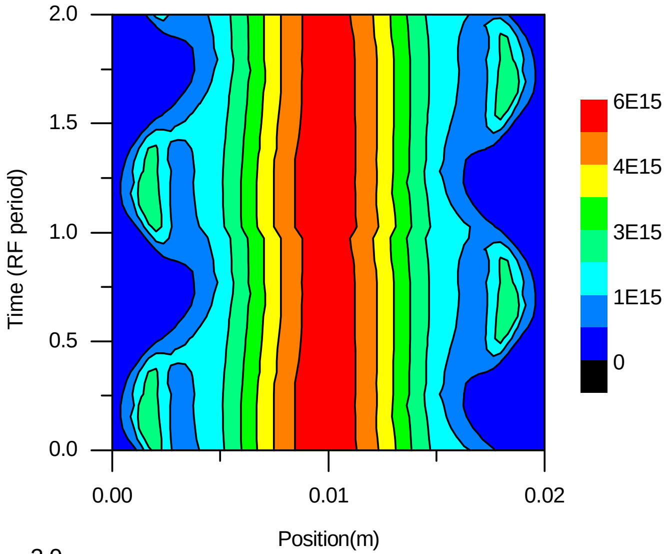
$$\frac{\partial \overrightarrow{E}^{s}_{eff}}{\partial t} = -\nu_m(\overrightarrow{E}^{s}_{eff} - \overrightarrow{E})$$

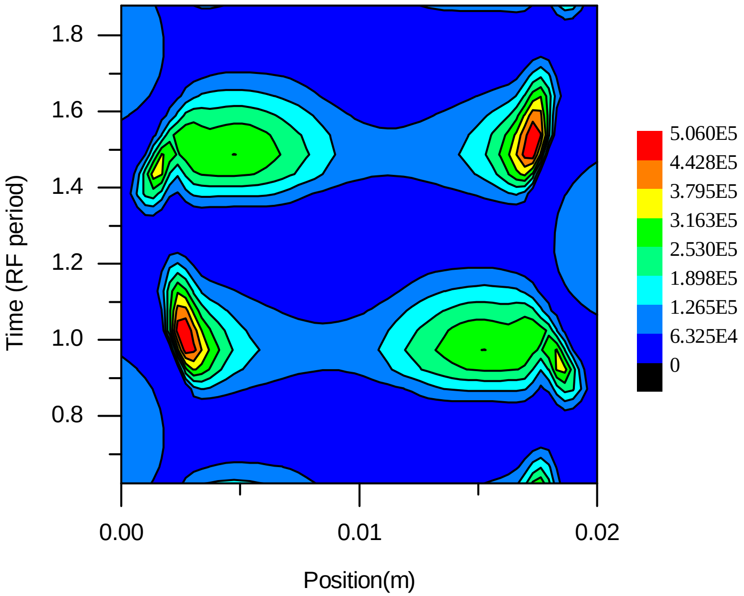
TABLE 1. Reaction model used to describe the chemistry of small molecular species in H_2/SiH_4 RF discharges.

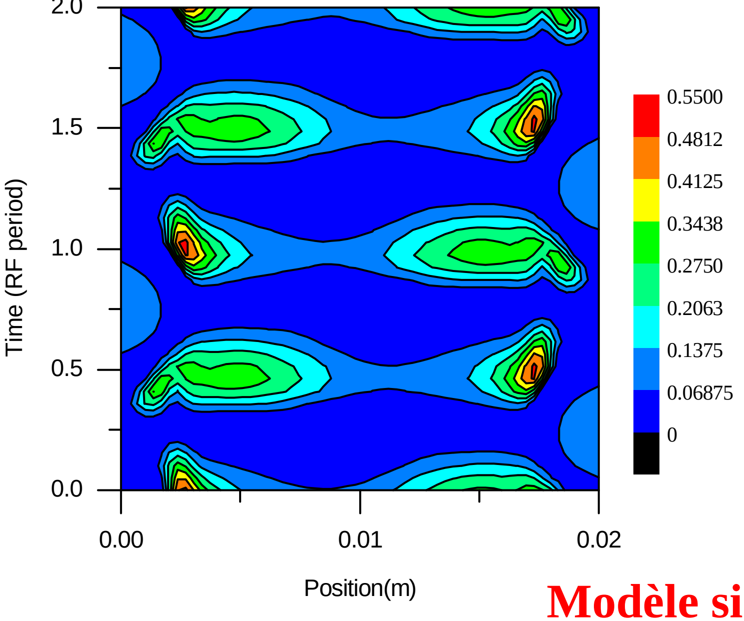
Reaction	Reference	Reaction	Reference
$e^- + H_2(v{=}0) \rightarrow e^- + H_2(v{=}1)$	(R1) [3]	$H_2^+ + H \rightarrow H^+ + H_2$	(R25) [4]
$e^- + H_2(v{=}0) \rightarrow e^- + H_2(v{=}2)$	(R2) [3]	$H_2 + H_2^+ \rightarrow H_3 + H$	(R26) [4]
$e^- + H_2(v{=}0) \rightarrow e^- + H_2(v{=}3)$	(R3) [3]	$H + H^- \rightarrow e^- + 2H$	(R27) [4]
$e^- + H_2(v{=}0) \rightarrow e^- + H_2(v{=}4)$	(R4) [3]	$H + H^- \rightarrow e^- + H_2$	(R28) [4]
$e^- + H_2(v{=}0) \rightarrow e^- + H_2(v{=}5)$	(R5) [3]	$H^+ + H_2 \rightarrow H_2^+ + H$	(R29) [4]
$e^- + H_2 \rightarrow 2e^- + H_2^+$	(R6) [3]	$H^+ + H^- \rightarrow 2H$	(R30) [4]
$e^- + H_2 \rightarrow e^- + 2H$	(R7) [3, 5]	$H^+ + 2H_2 \rightarrow H_3^+ + H_2$	(R31) [4]
$e^- + H \rightarrow 2e^- + H^+$	(R8) [6]	$H^- + H_2^+ \rightarrow H_2 + H$	(R32) [4]
$e^- + H_3^+ \rightarrow 3H$	(R9) [7]	$H^- + H_3^+ \rightarrow 2H_2$	(R33) [4]
$e^- + H_3^+ \rightarrow H + H_2$	(R10) [7]	$SiH_3^- + SiH_2^+ \rightarrow SiH_3 + SiH_2$	(R34) [8, 9]
$e^- + H_3^+ \rightarrow e^- + H^+ + 2H$	(R11) [6]	$SiH_3^- + H_2^+ \rightarrow SiH_3 + H_2$	(R35) [8, 9]
$e^- + H_2(v{=}4) \rightarrow H^- + H$	(R12) [5, 10]	$e^- + SiH_4 \rightarrow SiH_2^- + H_2$	(R36) [8, 9]
$e^- + H_2(v{=}5) \rightarrow H^- + H$	(R13) [5, 10]	$e^- + SiH_4 \rightarrow SiH_3^+ + H + 2e^-$	(R37) [8, 9]
$e^- + H_2(v{=}6) \rightarrow H^- + H$	(R14) [5, 10]	$SiH_3^- + H_3^+ \rightarrow SiH_3 + H_2 + H$	(R38) [8, 9]
$e^- + H_2(v{=}7) \rightarrow H^- + H$	(R15) [5, 10]	$SiH_3^- + H^+ \rightarrow SiH_3 + H$	(R39) [8, 9]
$e^- + H_2^+ \rightarrow e^- + H^+ + H$	(R16) [6]	$SiH_3^- + SiH_3^+ \rightarrow SiH_3 + SiH_3$	(R40) [8, 9]
$e^- + H_2^+ \rightarrow 2H$	(R17) [6]	$SiH_2^- + SiH_2^+ \rightarrow SiH_2 + SiH_2$	(R41) [8, 9]
$e^- + H^- \rightarrow 2e^- + H$	(R18) [6]	$SiH_2^- + H_2^+ \rightarrow SiH_2 + H_2$	(R42) [8, 9]
$e^- + SiH_4 \rightarrow 2e^- + SiH_2^+ + 2H$	(R19) [8, 9]	$SiH_2^- + H_3^+ \rightarrow SiH_2 + H_2 + H$	(R43) [8, 9]
$e^- + SiH_4 \rightarrow e^- + SiH_3 + H$	(R20) [8, 9]	$SiH_2^- + H^+ \rightarrow SiH_2 + H$	(R44) [8, 9]
$e^- + SiH_4 \rightarrow e^- + SiH_2 + 2H$	(R21) [8, 9]	$SiH_2^- + SiH_3^+ \rightarrow SiH_2 + SiH_3$	(R45) [8, 9]
$e^- + SiH_4 \rightarrow e^- + SiH_4(v{=}1)$	(R22) [8, 9]	$H + SiH_4 \rightarrow SiH_3 + H_2$	(R46) [8, 9]
$e^- + SiH_4 \rightarrow e^- + SiH_4(v{=}2)$	(R23) [8, 9]	$H_2 + SiH_2 \rightarrow SiH_4$	(R47) [8, 9]
$e^- + SiH_4 \rightarrow SiH_3^- + H$	(R24) [8, 9]		

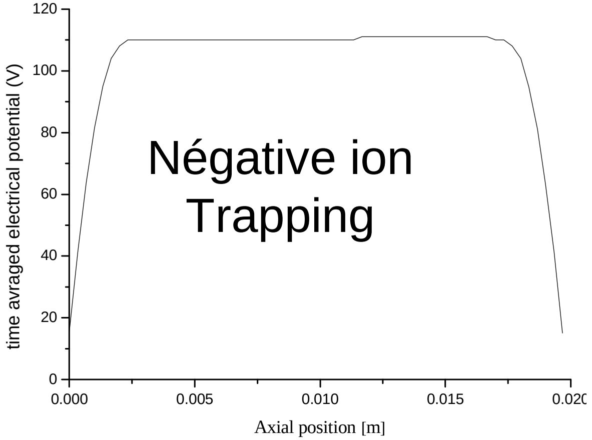
Dynamic of charged species

Dynamique des électrons : Fraction molaire et température

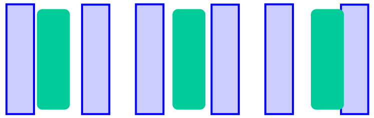








Négative ion Trapping

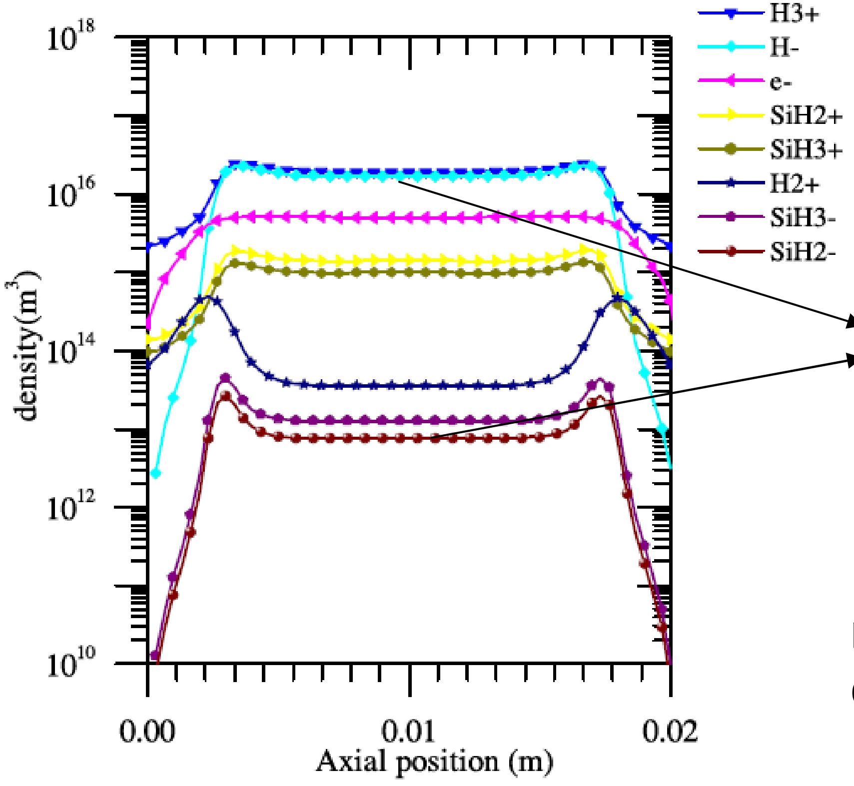


Modèle simple : nuage uniforme oscillant

Typical results

Feed gas: H_2/SiH_4 mixture (2% SiH_4 , 98% H_2)
Excitation voltage : 100 – 500 V
Pressure : 0.5 – 2 Torr

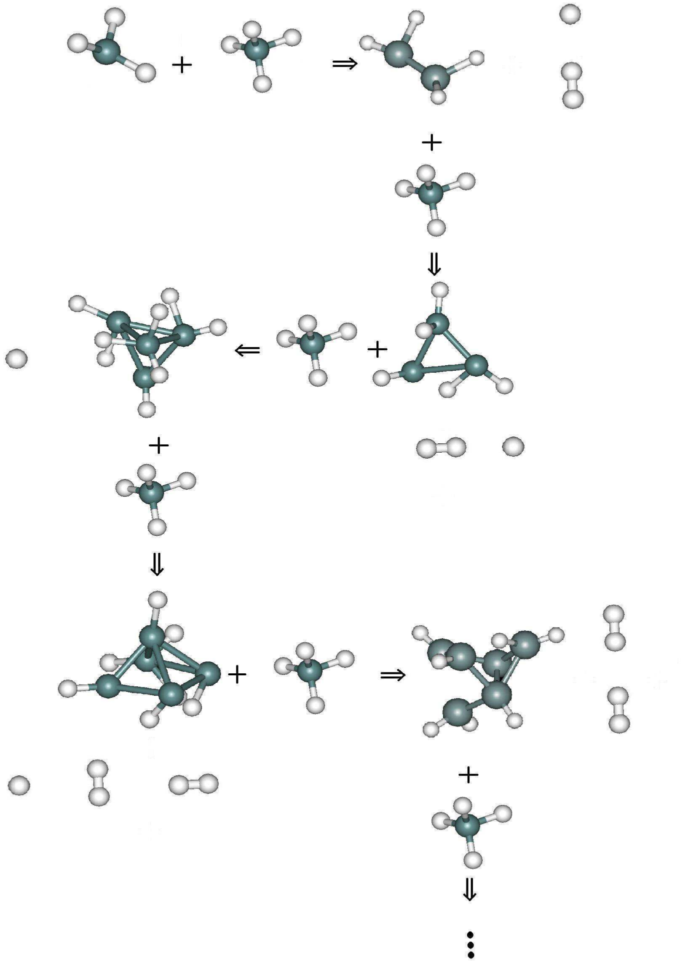
Time averaged species density



Negative ion trapping

Use SiH_3^- and SiH_2^- as input for molecular dynamic calculation of cluster growth

Growth of Si_nH_m clusters in a plasma reactor



Using our results from the plasma modeling, we now can follow the dynamics of the cluster growth as a result of the consecutive capture of plasma radials (SiH_4, SiH_3, SiH_2…).

APPROXIMATIONS IN OUR MOLECULAR DYNAMICS CODE

At each time step in our MD calculation, we solve the Schrödinger equation ("on the fly"):

$$H_{tot}\Psi = E\Psi$$

$$H_{tot} = \sum_{A}\sum_{\angle B}\frac{Z_A Z_B}{r_{AB}} - \sum_{A}\sum_{i}\frac{Z_A}{r_{Ai}} + \sum_{i}\sum_{\angle j}\frac{1}{r_{ij}} - \frac{\hbar}{2\pi.m}\sum_{i}\nabla_i^2 - \frac{\hbar}{2\pi.M_A}\sum_{A}\nabla_A^2$$

For our system, it is impossible to solve Schrödinger's equation directly. Therefore, we employed the semi-empirical PM3 method to calculate the electronic structure of our system; e.g., we used three approximations for solving the electronic Schrödinger equation
(reference: J.J.P. Stewart, J. Comput. Chem. **10** (1989) 209 and 221):

1) The Born-Oppenheimer's approximation :

$$H_{tot} = \sum_{A}\sum_{\angle B}\frac{Z_A Z_B}{r_{AB}} - \sum_{A}\sum_{i}\frac{Z_A}{r_{Ai}} + \sum_{i}\sum_{\angle j}\frac{1}{r_{ij}} - \frac{\hbar}{2\pi.m}\sum_{i}\nabla_i^2$$

APPROXIMATIONS IN OUR MOLECULAR DYNAMICS CODE

2) The wave function can be written as a Slater determinant.

$$\Psi = (n!)^{-1/2} \left| \Psi_p^{\alpha}(1) \Psi_p^{\beta}(2) \ldots \Psi_z^{\alpha}(n-1) \Psi_z^{\beta}(n) \right|$$

where $\Psi_p^{\alpha}(1)$ is a p wave function for an electron with α spin

3) LCAO approximation:

$$\Psi_p(i) = \frac{1}{\sqrt{N_p}} \sum_k c_k^p \Phi_k(i)$$

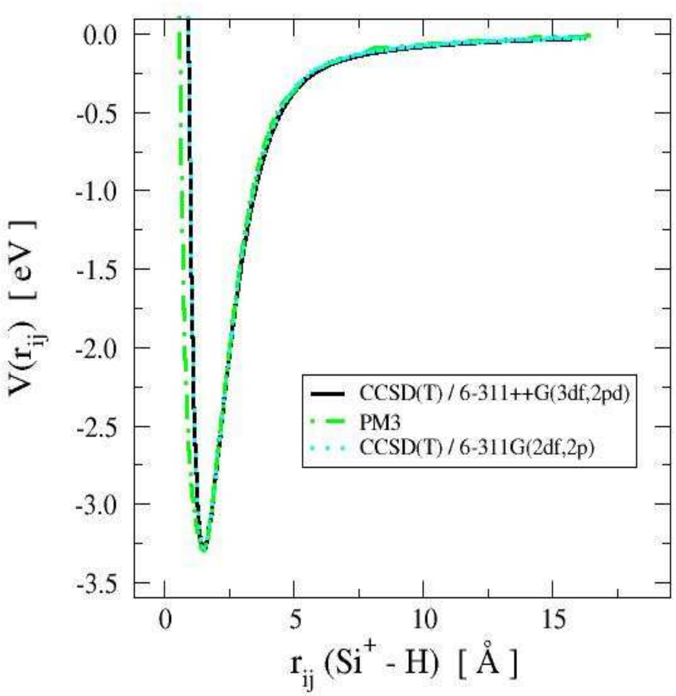
$$N_p = \sum_k \sum_l c_k^p c_l^p S_{kl}$$

Where S_{kl} is the integral overlap beetwen k and l.

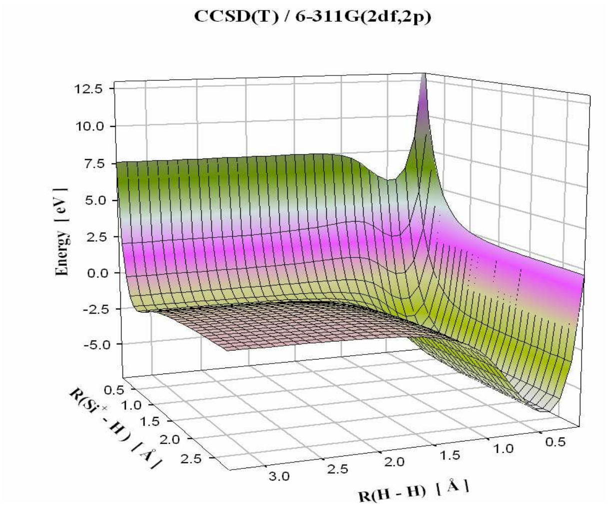
Within the PM3 method, we use s, p_x, p_y, p_z as basis set.

Comparison to ab intio calculations

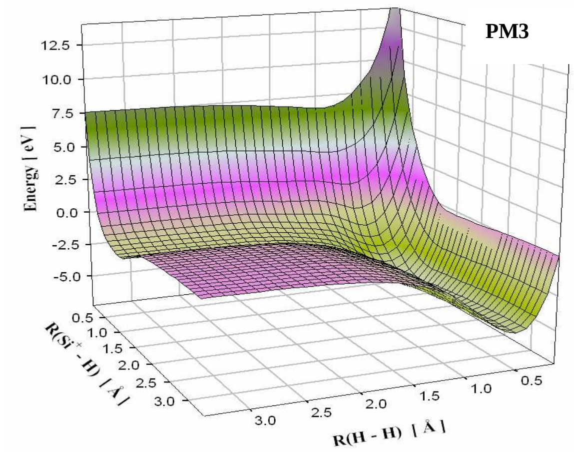
Validation of our PM3 semiempirical method in comparison to ab initio coupled cluster CCSD(T) calculations.



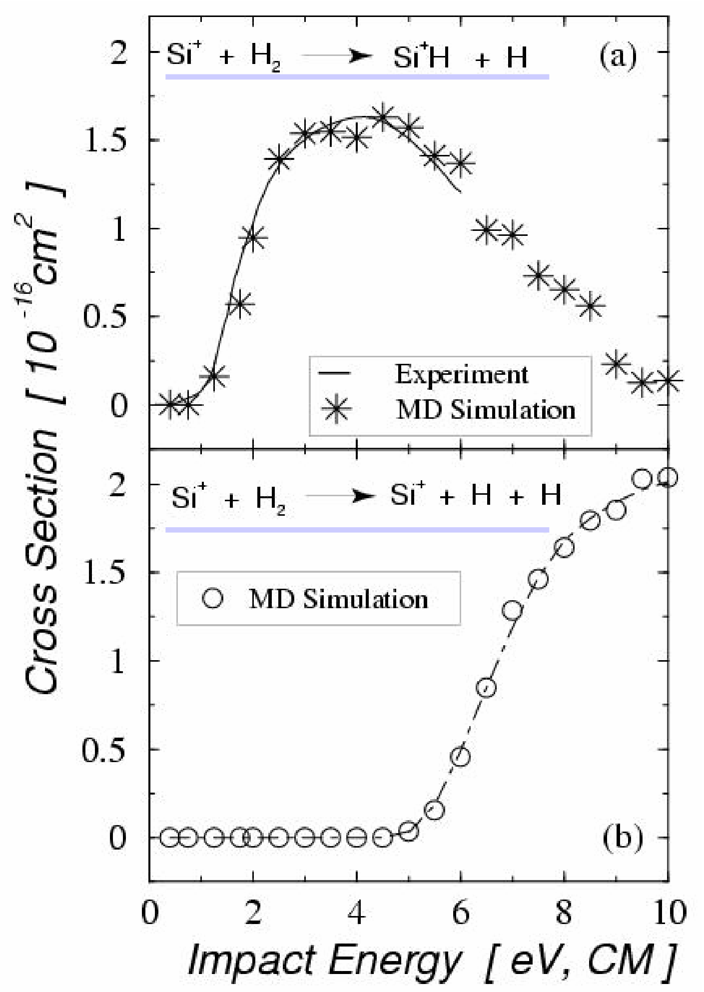
Si$^+$ - H



H - Si$^+$ - H



Experimental and calculated reactive cross sections



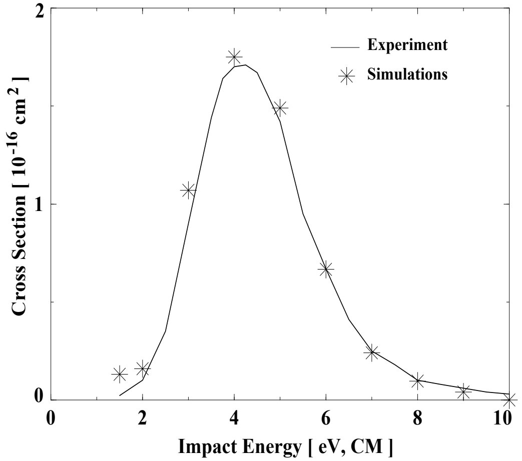
Experiments by Armentrout et al.

$Si^+(^2P)$ + H_2

Reactive cross section as function of kinetic impact energy

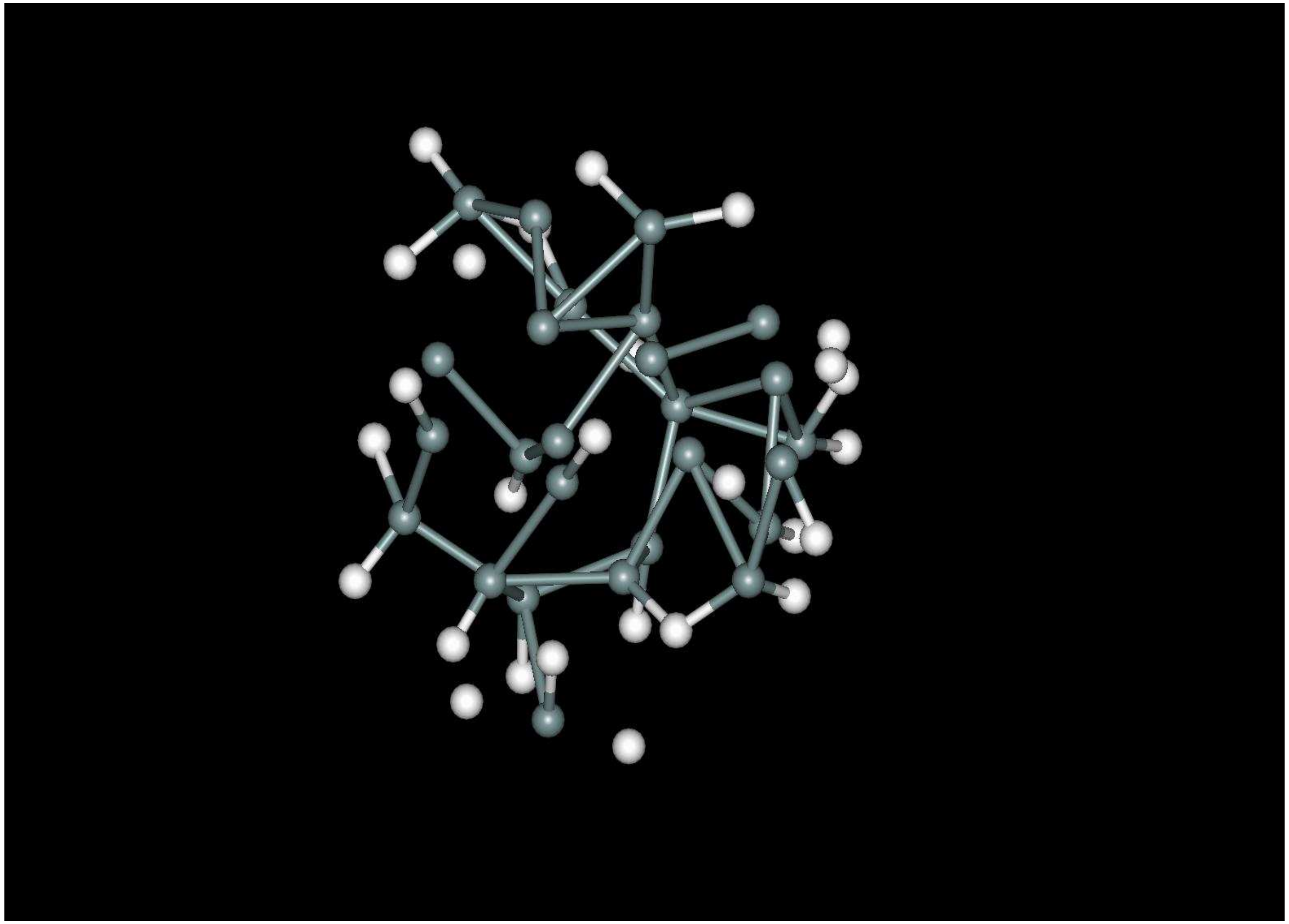
(a) for SiH^+ production and

(b) for complete dissociation.



$Si^+ + SiH_4 \longrightarrow Si_2H^+ + 3H$

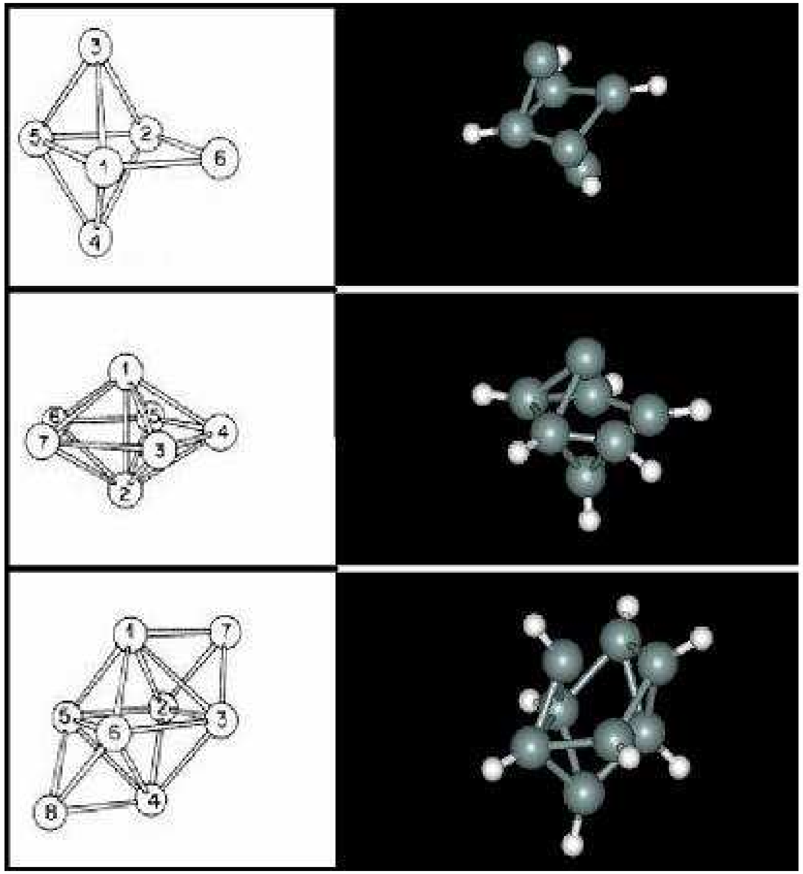
Growth of $Si_n H_m$ clusters in a plasma reactor



Under realistic SiH_4 plasma conditions, we always find amorphous nanostructures

Growth of Si_n H_m clusters in a plasma reactor

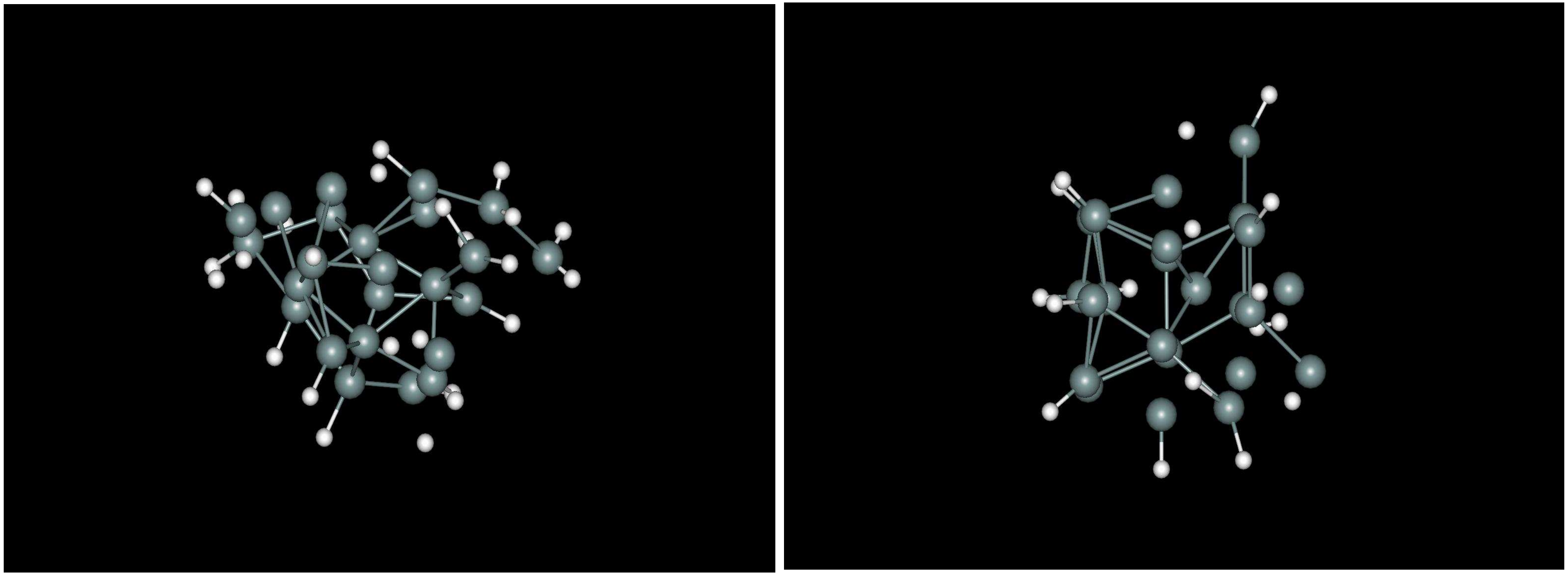
Using relatively high kinetic impact energies of about 2eV, we always find structures that contain very little hydrogen and that are very similar to those structures predicted by K. Raghavachari for small Si_n clusters via ab-initio calculations (J. Chem. Phys. 84, 5672 [1986]).



E_{kin} ~2eV

Growth of $Si_n H_m$ clusters in a plasma reactor

Role of atomic H for the crystallization of an amorphous $Si_{24}H_{25}$ nanoparticle

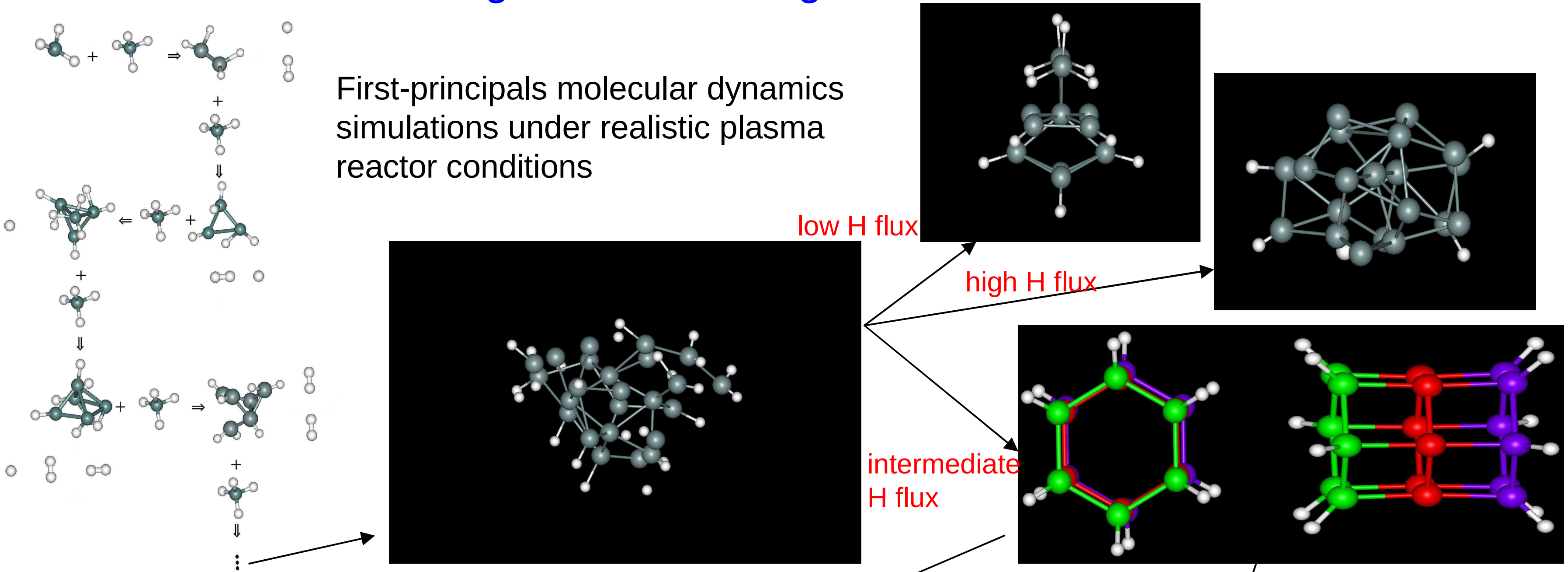


BEFORE … ***AFTER …***

… the collision with 10 thermal H atoms

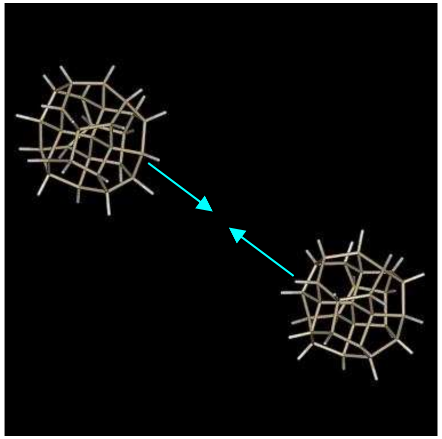
Atomic-scale simulation of nanocluster growth, crystallization, & deposition

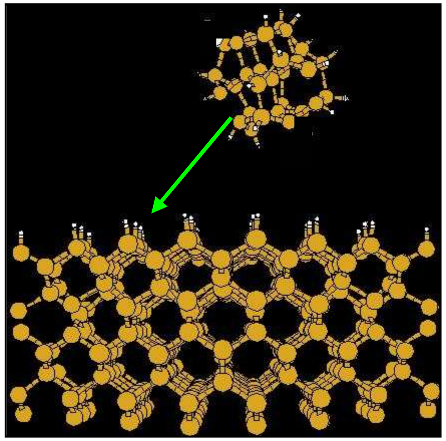
Ning NING and Holger VACH



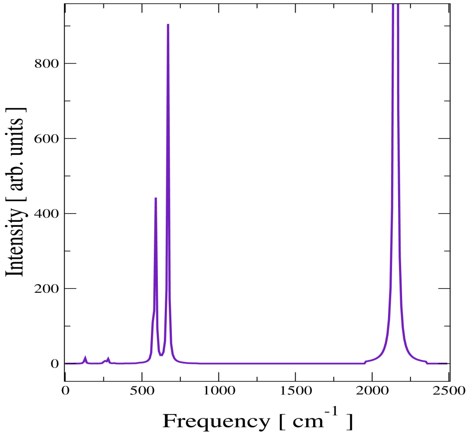
First-principals molecular dynamics simulations under realistic plasma reactor conditions

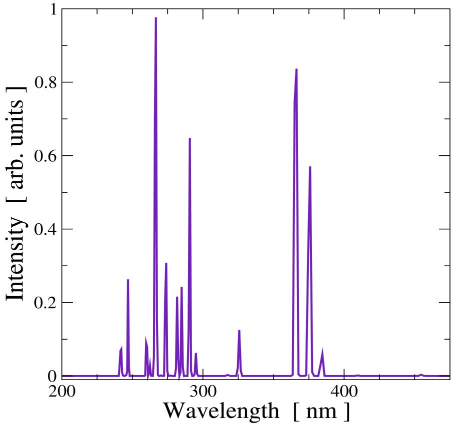
Model-potential molecular dynamics simulations





Ab-initio theoretical spectroscopy





Conclusion

Complex processes → governing step → key process

H-atom often involved

Plasma/surface interaction : Ion

Gas phase generated positive ions :

Birth :

Mainly in the bulk :

Electron-impact ionisation on the parent molecules

Energy threshold : >10 eV

Transport :

ambipolar diffusion in the bulk

Acceleration in the sheath = f(density)

➔$\lambda_{ion} >> \lambda_{sh}$ ➔ directional fluxes with very high drift energy ➔ implantation and sputtering

➔$\Lambda_{ion} << \lambda_{sh}$ ➔ collision with neutral ➔ energy sharing with neutral ➔ fast neutral moderatly accelerated ions

Fate on the surface

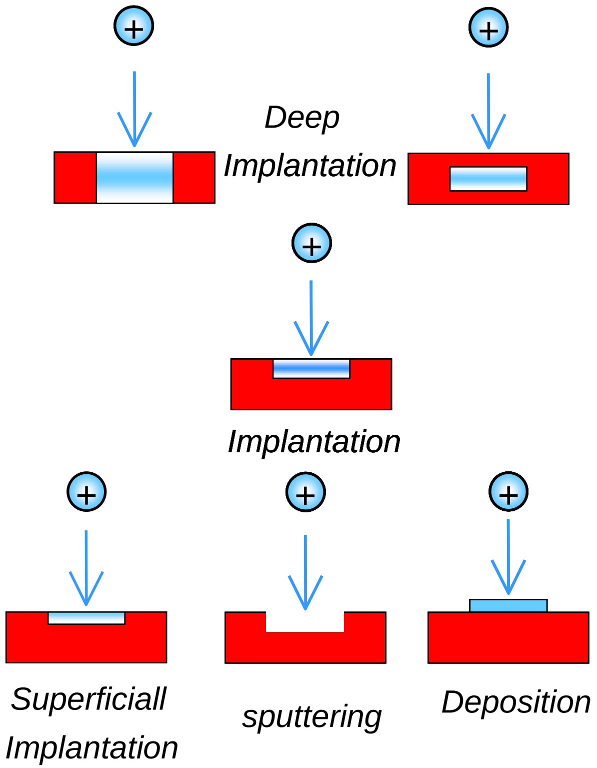
➔$\lambda_{ion} >> \lambda_{sh}$ ➔ implantation and sputtering

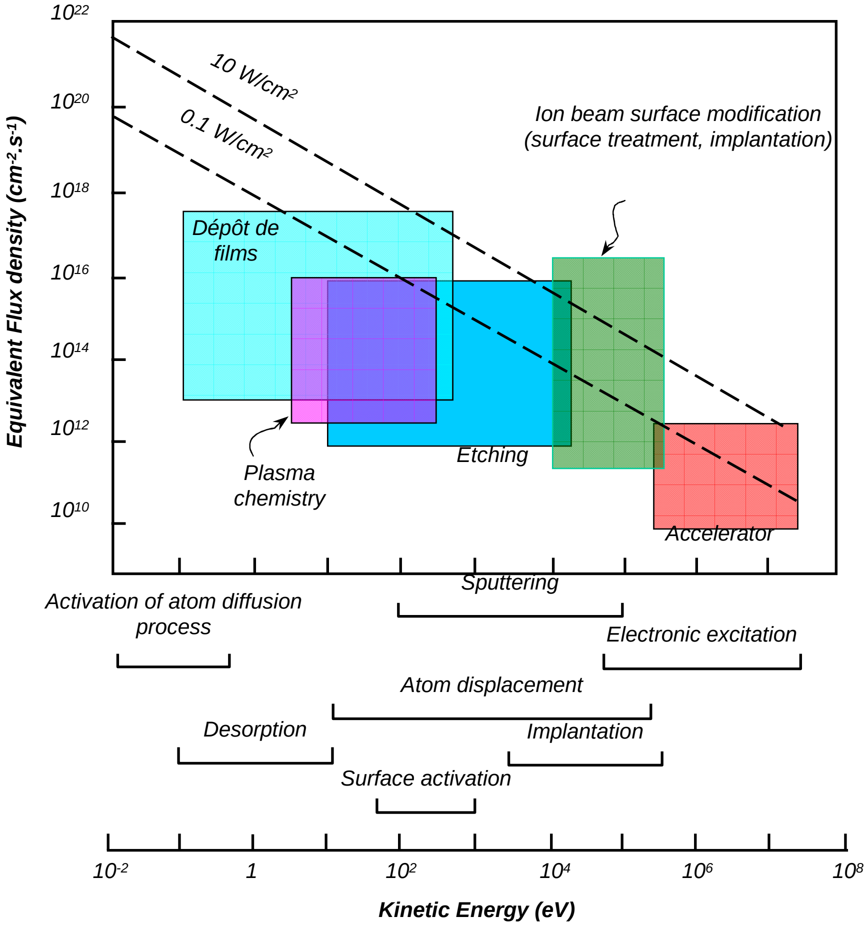
➔$\Lambda_{ion} << \lambda_{sh}$ ➔ sputtering, Auger emission, chemistry

Plasma/surface interaction : Ions

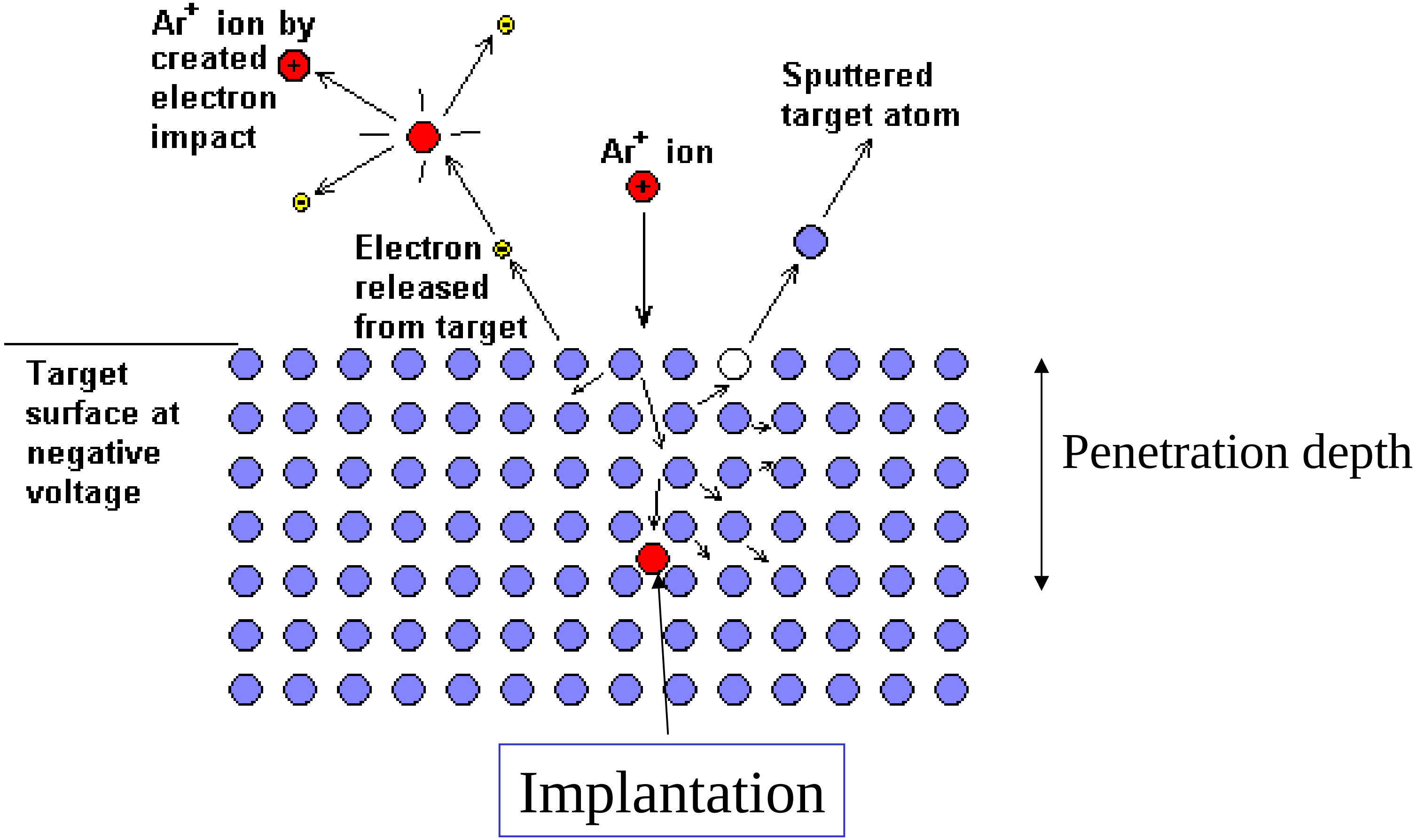
High Energy

Low energy





Plasma/surface interaction : Ions

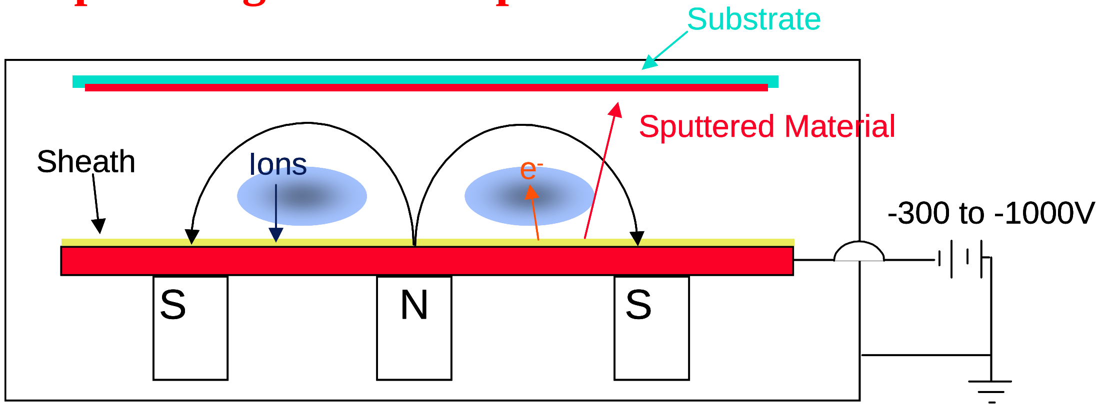


Plasma/surface interaction : ions – sputtering

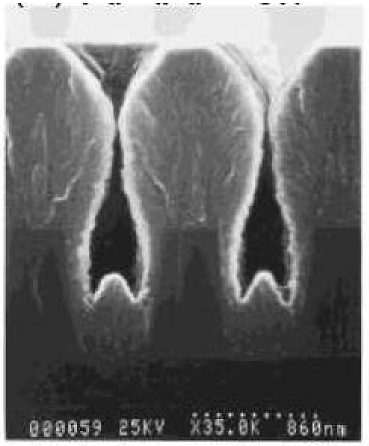
Magnetron or DC Sputtering

➔Extract atoms from a massive target to deposit a thin film on a substrate

the case of magnetron sputtering assisted deposition

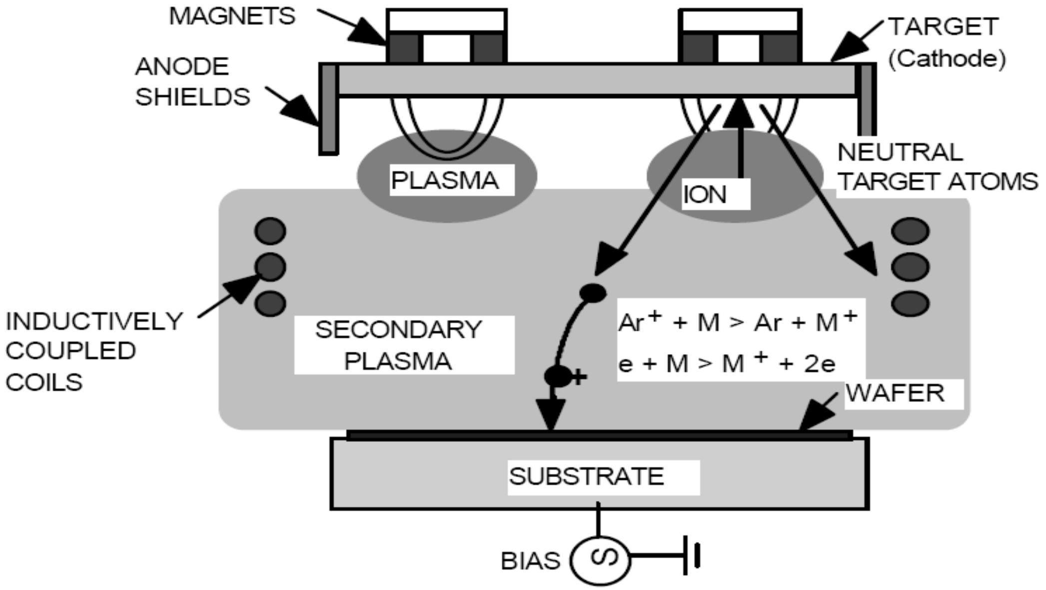


- Ion sputtering
- Mainly Neutral driven deposition



Metalization in Microelectronic
Al deposition into trenches ➔
Detrimental Void formation
Hamaguchi and S. M. Rossnagel, J. Vac. Sci. Technol. B **13**, 183 (1995).

Plasma/surface interaction : ions – sputtering

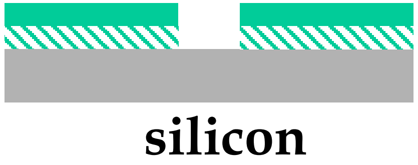


IPVD
Ion sputtering
Then
Secondary ionization
➔ ion + atom deposition

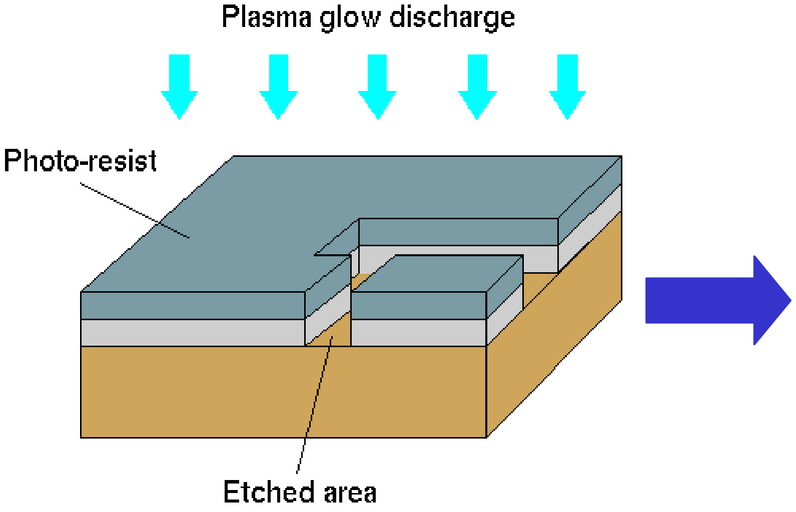
Synergetic effects between positive ion and neutral in etching
The example of material processing in microelectronic

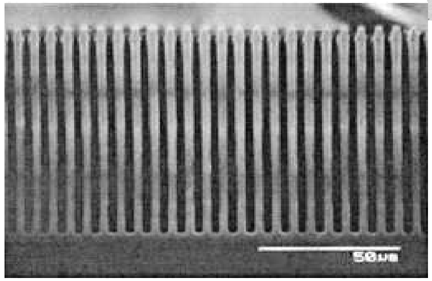
Microelectronic :
« Etching » Define the microscopic feature of electronic circuits
Anisotropic etching is needed

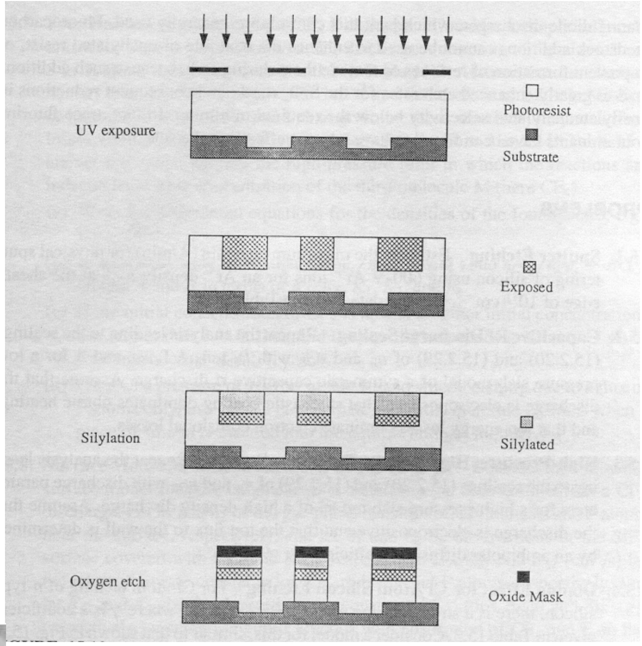
Wet



Dry



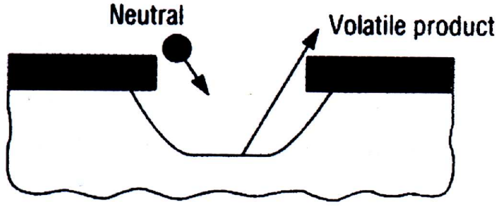




Lieberman and Lichtenberg
Principle of plasma discharges and material processing
Wiley(1994)

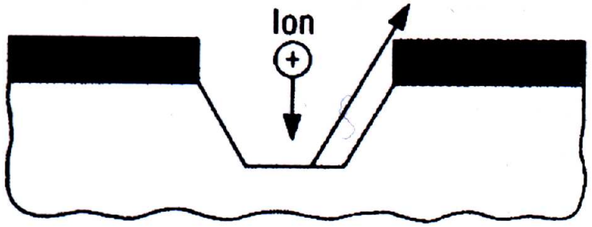
Plasma/surface interaction : Positive ions (+ neutral)

Isotropic chemical etching/deposition



+

Ion sputtering

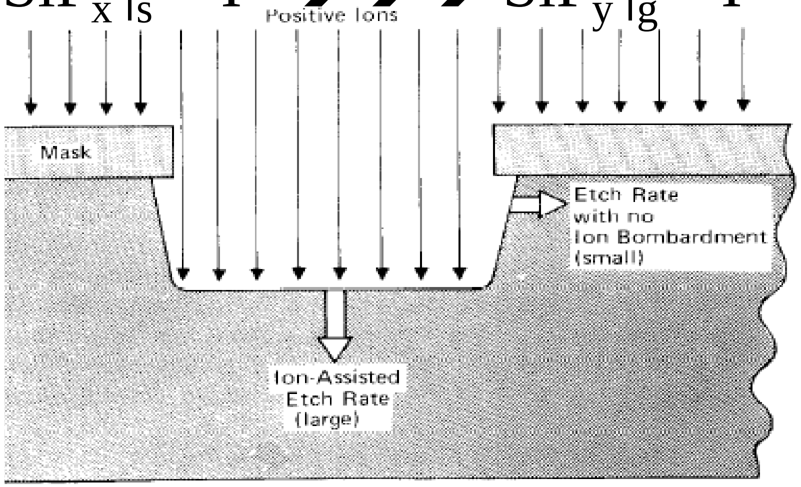


SF_6 based Ion assisted etching

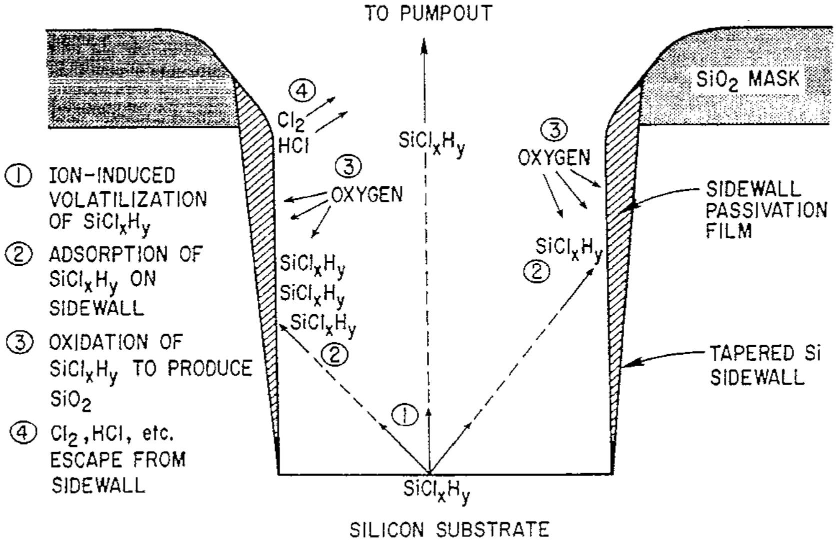
$\mathrm{Si} + x\mathrm{F} \rightarrow\rightarrow \mathrm{SiF}_x|_s$

$\mathrm{SiF}_x|_s \rightarrow \rightarrow \mathrm{SiF}_y|_g$

$\mathrm{SiF}_x|_s + \mathrm{I}^+ \rightarrow\rightarrow\rightarrow \mathrm{SiF}_y|_g + \mathrm{I}^+$



Plasma/surface interaction : Positive ions (neutral)



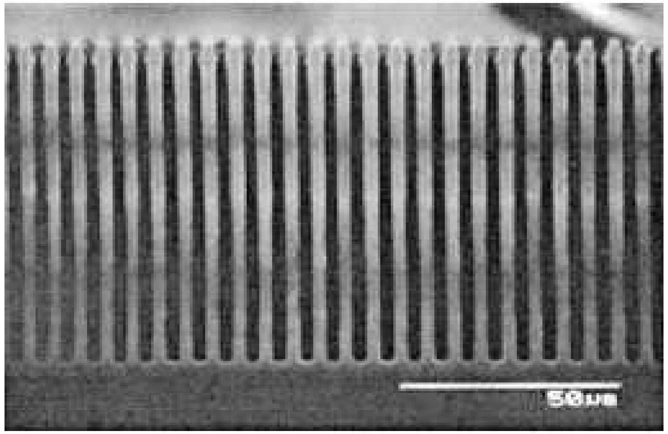
$HCl/O_2/BCl_3$ based etching

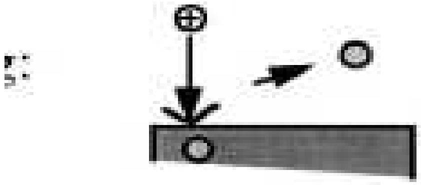
$Si + 4Cl \rightarrow SiCl_4|_g$ (Etching)

$Si + xO + yF \rightarrow SiF_xO_y$
(etching(x) vs depsosition(y))

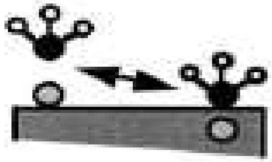
$Si + 2O \rightarrow SiO_2|_s$ (deposition)

Etching vs deposition + anisotropy = f(recipies, V_{bias}, Ts)

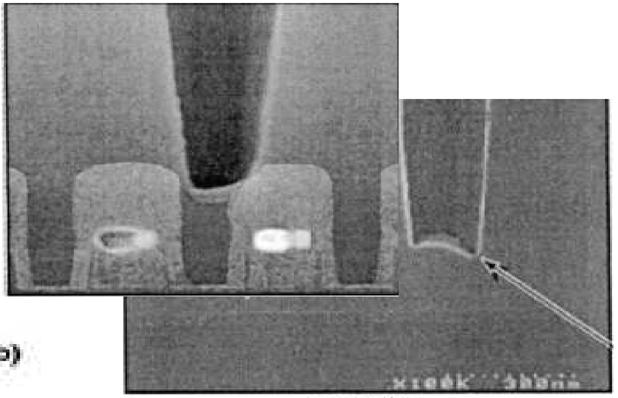




Ar$^+$ + e$^-$ + SiO$_2$(b) <--> SiO$_2$ + Ar



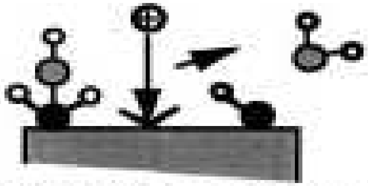
SiH$_3$ + Si(s) <--> SiH$_3$(s) + Si(b)



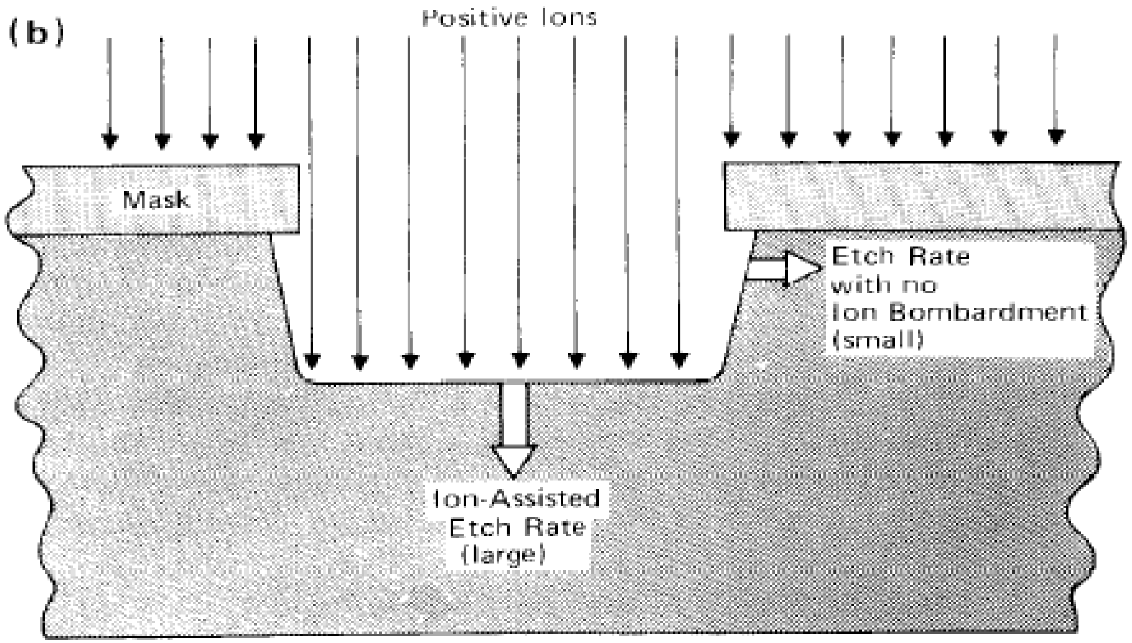
trenching

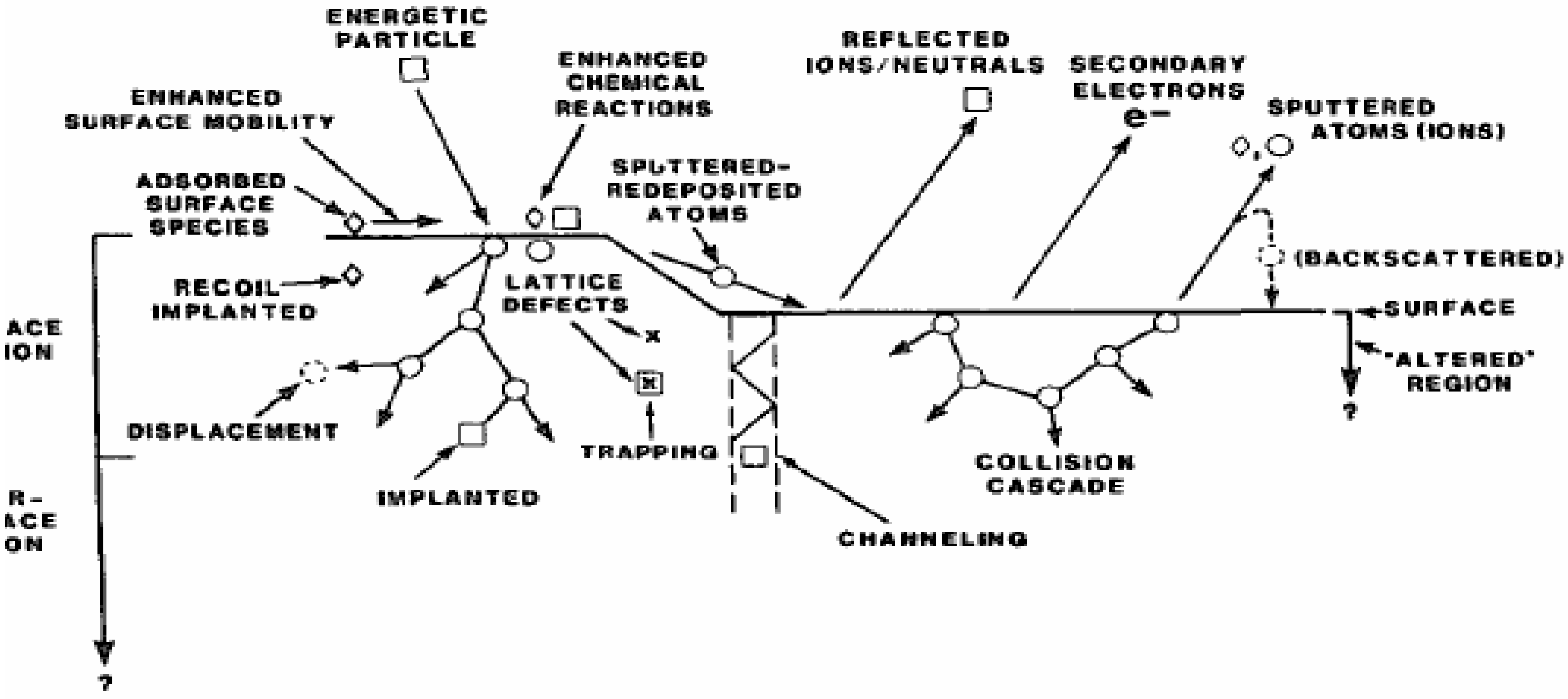
Ar$^+$ + e$^-$ <--> Ar

Reaction:

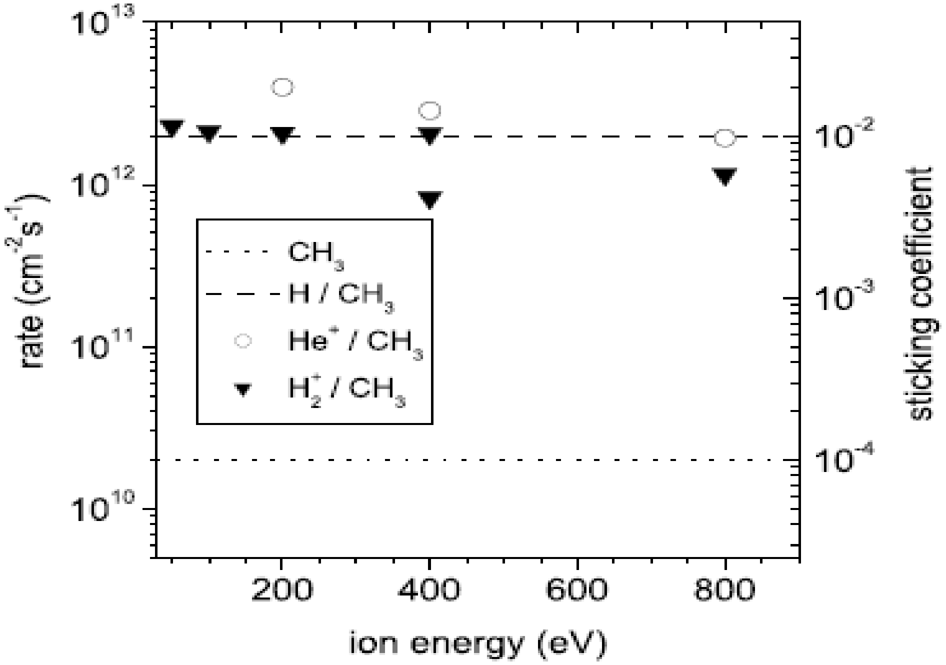


Ar$^+$ + e$^-$ + Si (OH)H$_2$(s) <-->SiH(s) + H$_2$O + Ar

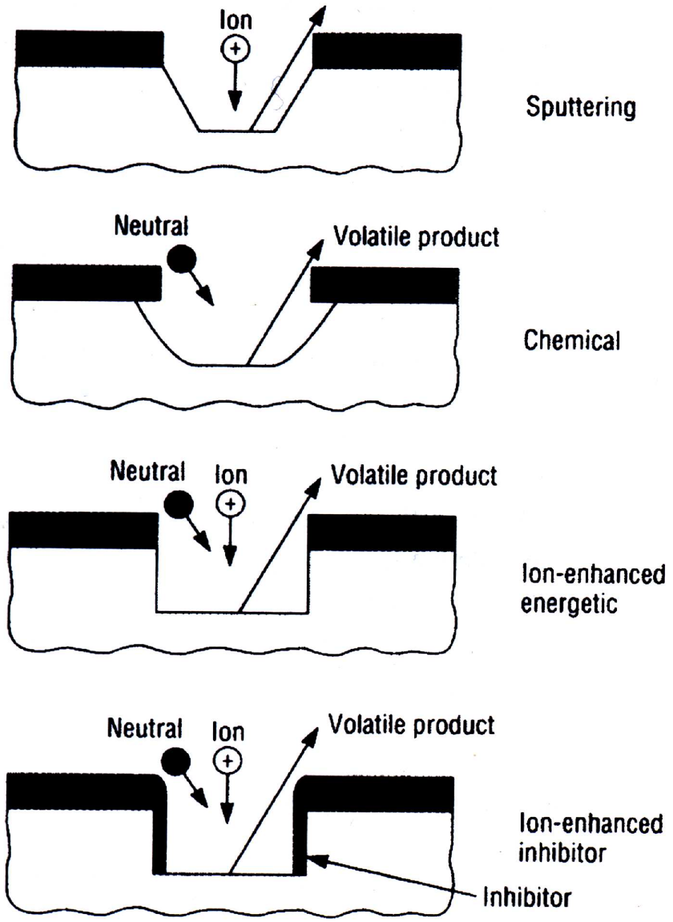

(b)
Positive Ions
Mask
Etch Rate
with no
Ion Bombardment
(small)
Ion-Assisted
Etch Rate
(large)

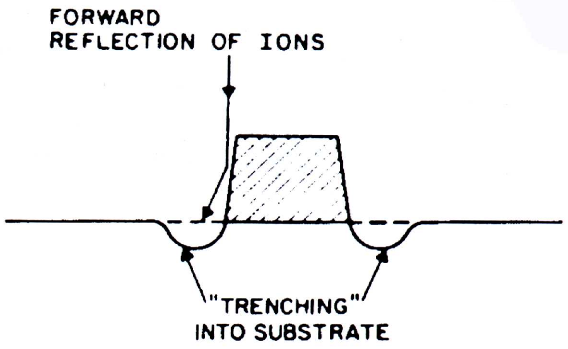


ENERGETIC PARTICLE
ENHANCED CHEMICAL REACTIONS
REFLECTED IONS/NEUTRALS
SECONDARY ELECTRONS
e−
SPUTTERED ATOMS (IONS)
ENHANCED SURFACE MOBILITY
ADSORBED SURFACE SPECIES
SPUTTERED-REDEPOSITED ATOMS
(BACKSCATTERED)
RECOIL IMPLANTED
LATTICE DEFECTS
x
SURFACE
"ALTERED" REGION
?
ACE
ION
DISPLACEMENT
TRAPPING
IMPLANTED
COLLISION CASCADE
CHANNELING
R-
ACE
ON
?



rate (cm^{-2}s^{-1})
10^{13}
10^{12}
10^{11}
10^{10}
sticking coefficient
10^{-2}
10^{-3}
10^{-4}
200
400
600
800
ion energy (eV)
CH$_3$
H / CH$_3$
He$^+$ / CH$_3$
H$_2^+$ / CH$_3$


Ion
Sputtering
Neutral
Volatile product
Chemical
Neutral
Ion
Volatile product
Ion-enhanced energetic
Neutral
Ion
Volatile product
Ion-enhanced inhibitor
Inhibitor


FORWARD REFLECTION OF IONS
"TRENCHING" INTO SUBSTRATE

Adsorption-Recombination assisted growth of diamond

C_2H_2 as growth species