Thomas Schwarz-Selinger

Erosion Processes (erosion of carbon by hydrogen)

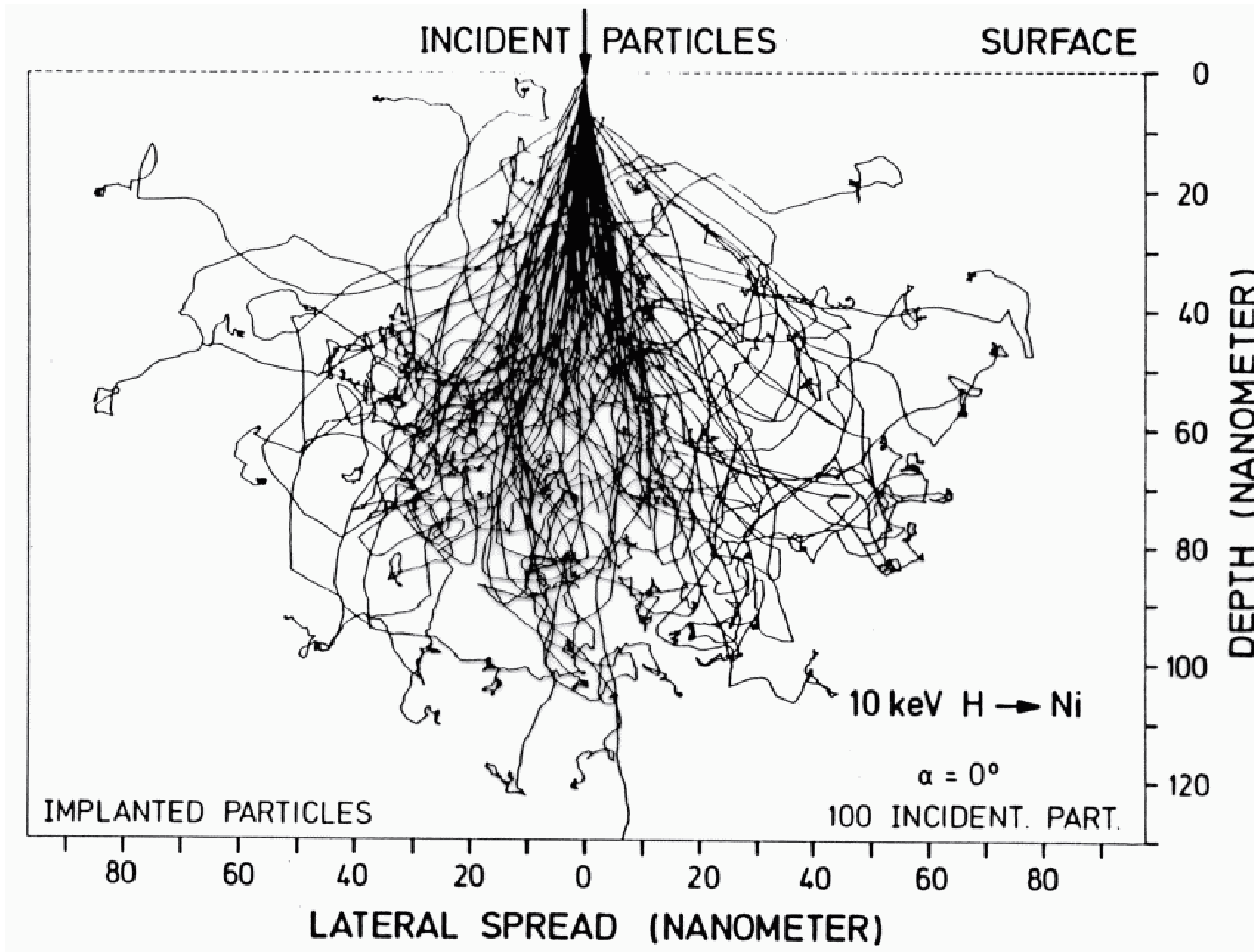
- Chemical erosion
- Physical sputtering
- **Chemical sputtering**

Codeposition

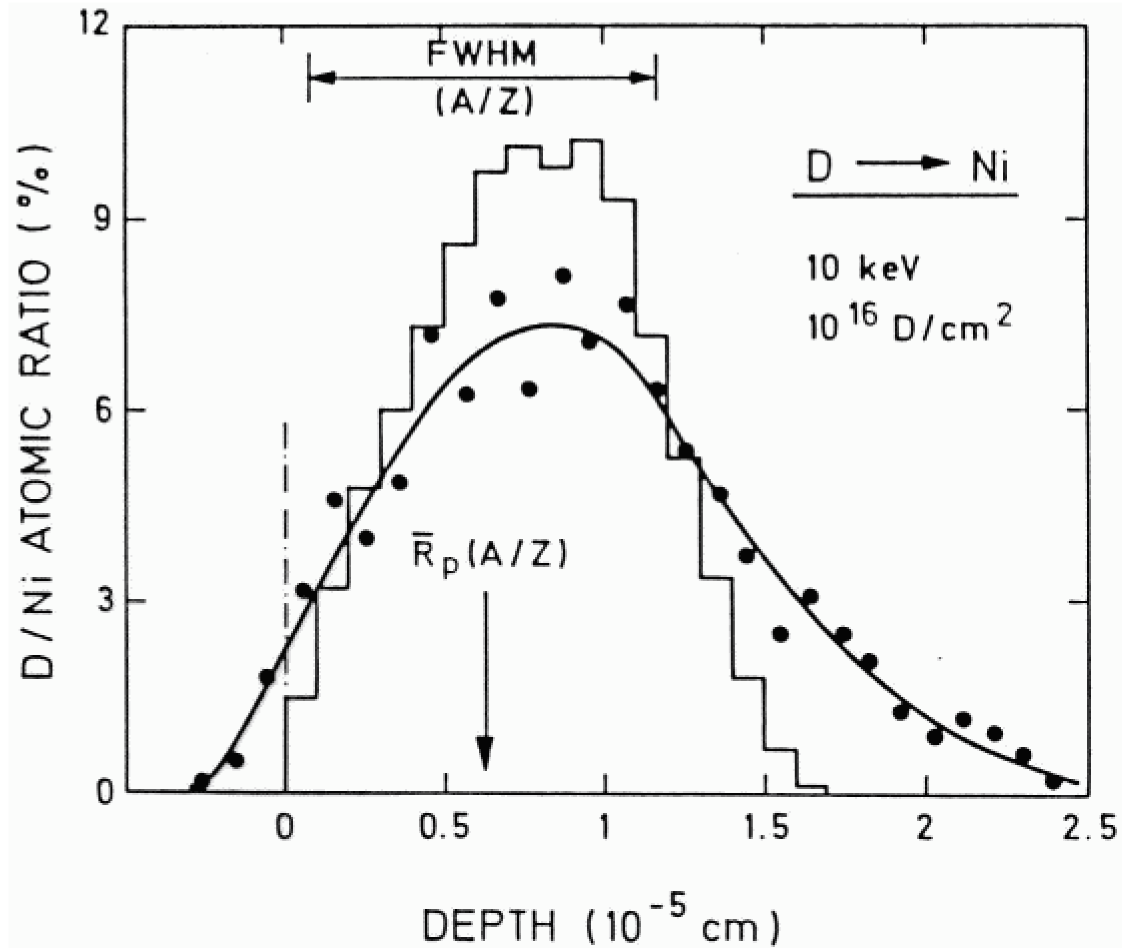
Implantation, diffusion and release

Collision cascade

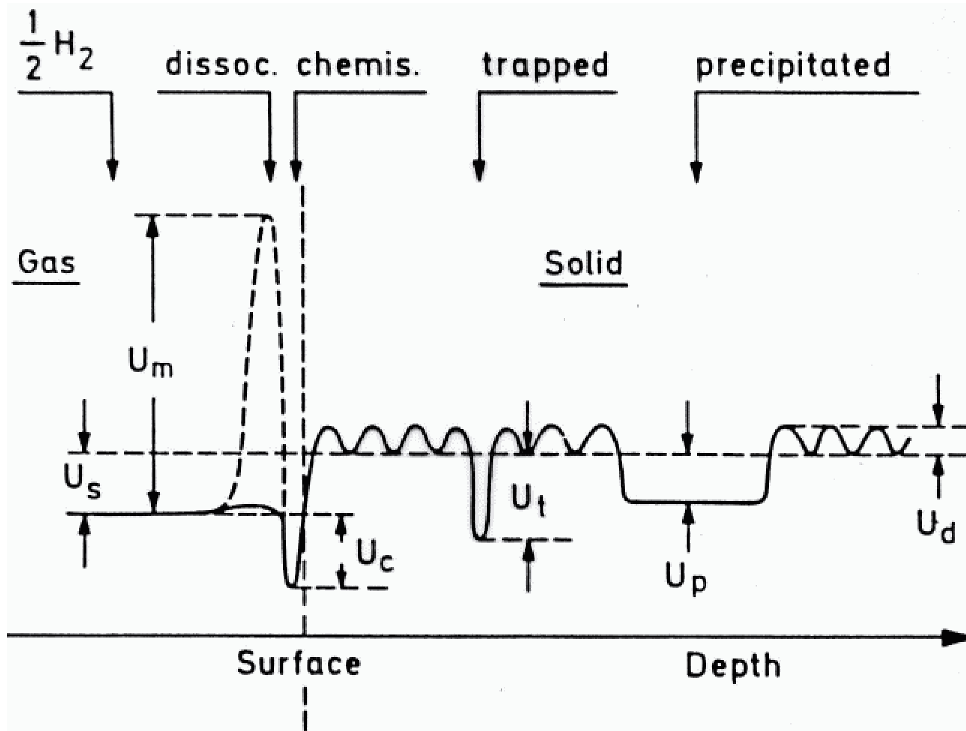
IPP



Range and range distribution



Schematic energy diagram for H in metals



Processes:

- Implantation, Diffusion, Trapping

$$\frac{\delta c_s}{\delta t} = D(t)\frac{\delta^2 c_s}{\delta x^2} + S(x,t) - T(c_s, c_t, x, t)$$

source term S from range distribution

$$D = D_0 e^{-\frac{U_d}{kT}}$$

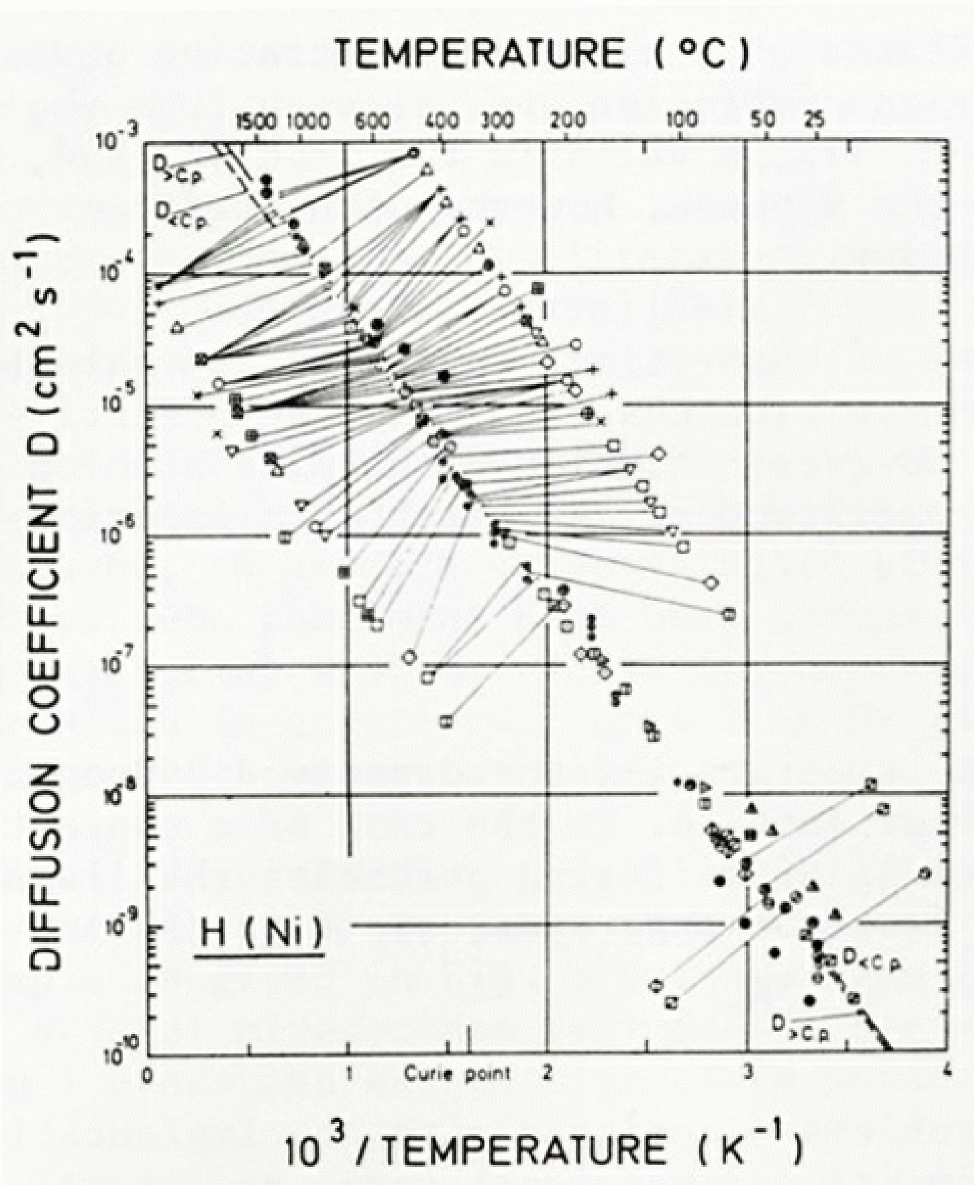
$$T = 4\pi r_d D\left[c_s\left(c_T - c_t\right) - N_H c_t e^{-\frac{U_t}{kT}}\right]$$

- Recombinative release

steady state fluxes $j_- = Kc_s(0)^2, \quad j_- = Kc_s(d)^2$

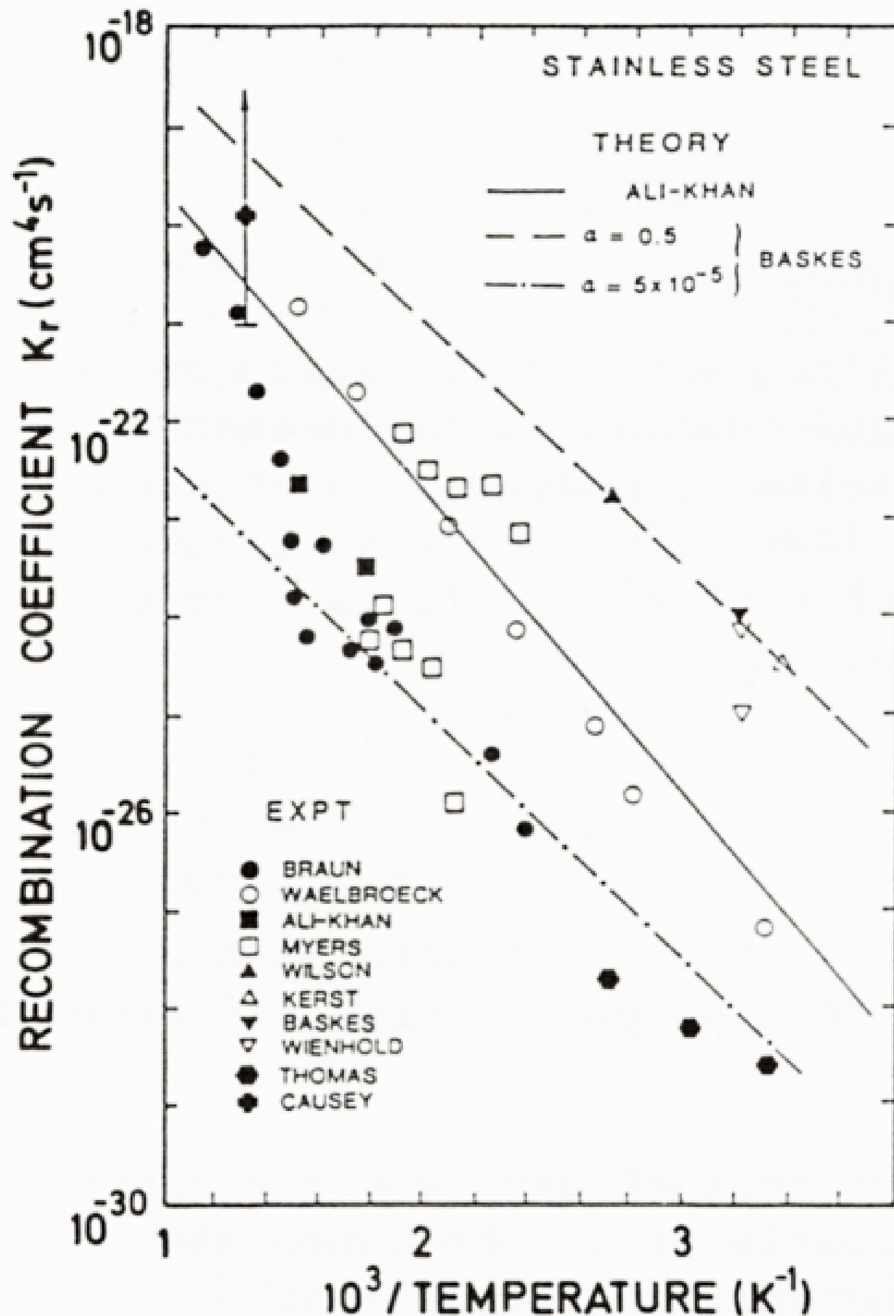
K recombination constant $K = \frac{K_0}{\sqrt{T}} e^{-\frac{U_r}{kT}}$

Diffusion coefficients



- For many metals very detailed data exist for the diffusion of hydrogen
- However, data are very scarce for the potential first wall materials W and Be
- as well as for non-metallic compounds

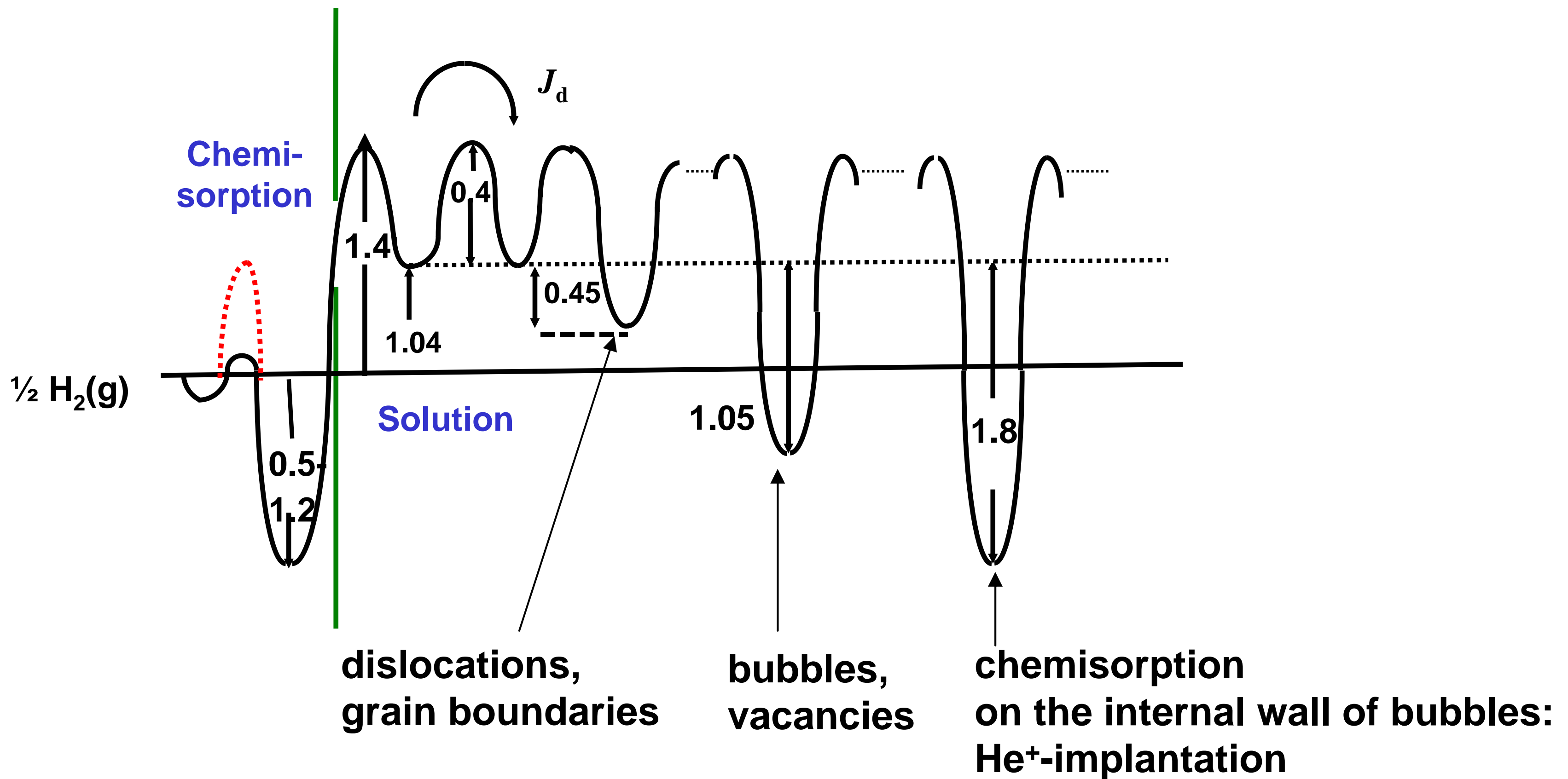
Recombination coefficient



Recombination coefficient for hydrogen in stainless steel

- acceptable data situation
- strong influence on surface conditions

Mechanism of deuterium behavior in polycrystalline W

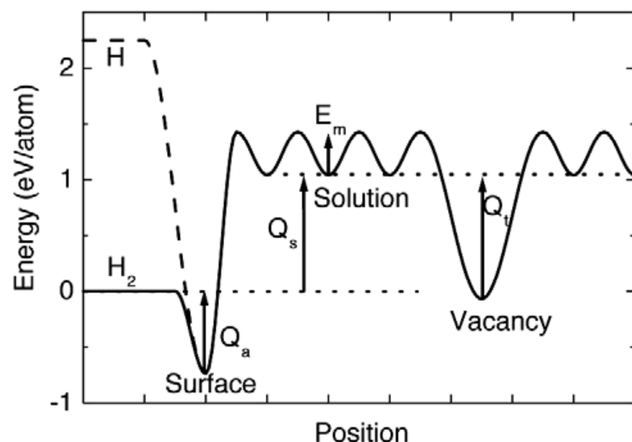


Influence of surface impurities on retention

IPP

In Tungsten:

Retention dominated by diffusion and trapping



No saturation at high fluences

Enhanced retention due to oxide and carbide surface layers

Retention [D/m^2]

1×10^{23}

10^{22}

10^{21}

10^{20}

100% retention

200 eV D+

WO_3

$\alpha\ \Phi^{1/2}$

pure W

10^{21} 10^{22} 1×10^{23} 10^{24} 1×10^{25}

Fluence [D/m^2]

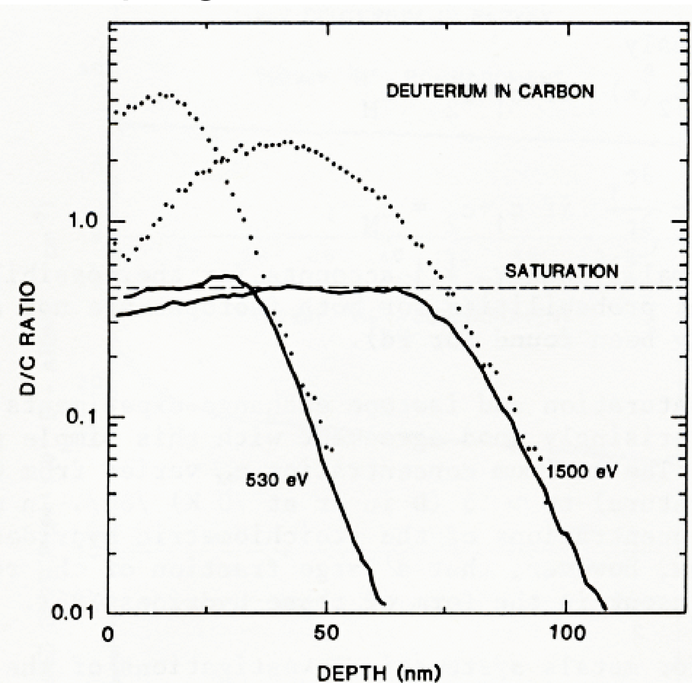
Mechanisms of Hydrogen retention in Carbon

IPP

In Carbon materials:

100% retention at low fluences

Saturation at high fluences, independent of doping



1 keV D^+

100% retention

$\alpha\,\Phi^{0.26}$

$\alpha\,\Phi^{0.15}$

Retained D (D/m^2)

Fluence Φ (D/m^2)

10^{20} 10^{21} 10^{22} 10^{23} 10^{24} 10^{25}

Pyrolytic graphite

isotropic graphites graphitised at 2100 to 2750°C

ungraphitised material

1000°C

Thomas Schwarz-Selinger, IAEA Workshop on Atomic and Molecular Data for Fusion Energy Research, August 28 - September 8, 2006, Abdus Salam International Centre for Theoretical Physics, Trieste

Mechanisms of Hydrogen retention: *Codeposition*

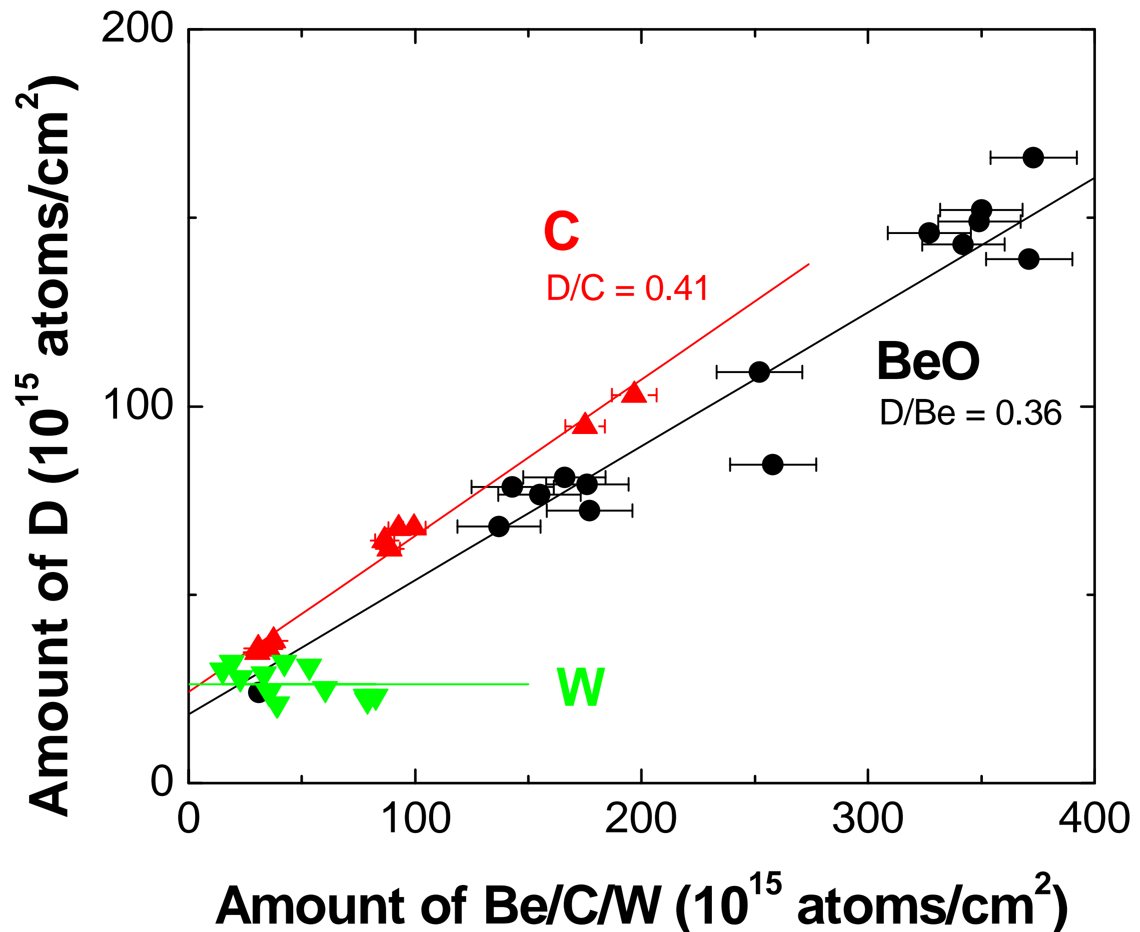
IPP

Simultaneous deposition and implantation:

investigated on collectors during sputtering

no saturation for Carbon materials (and BeO) due to continous supply of new material

no measurable codeposition for Tungsten (and Stainless Steel)



Nomenclature

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- **Chemical erosion** is a selective removal of surface atoms by ***chemical reactions***, forming volatile reactants that can desorb.

- **Physical sputtering** is the ***kinetic ejection of surface atoms*** by incident energetic ions or atoms ***due to collision processes***. (playing billiards with surface atoms).

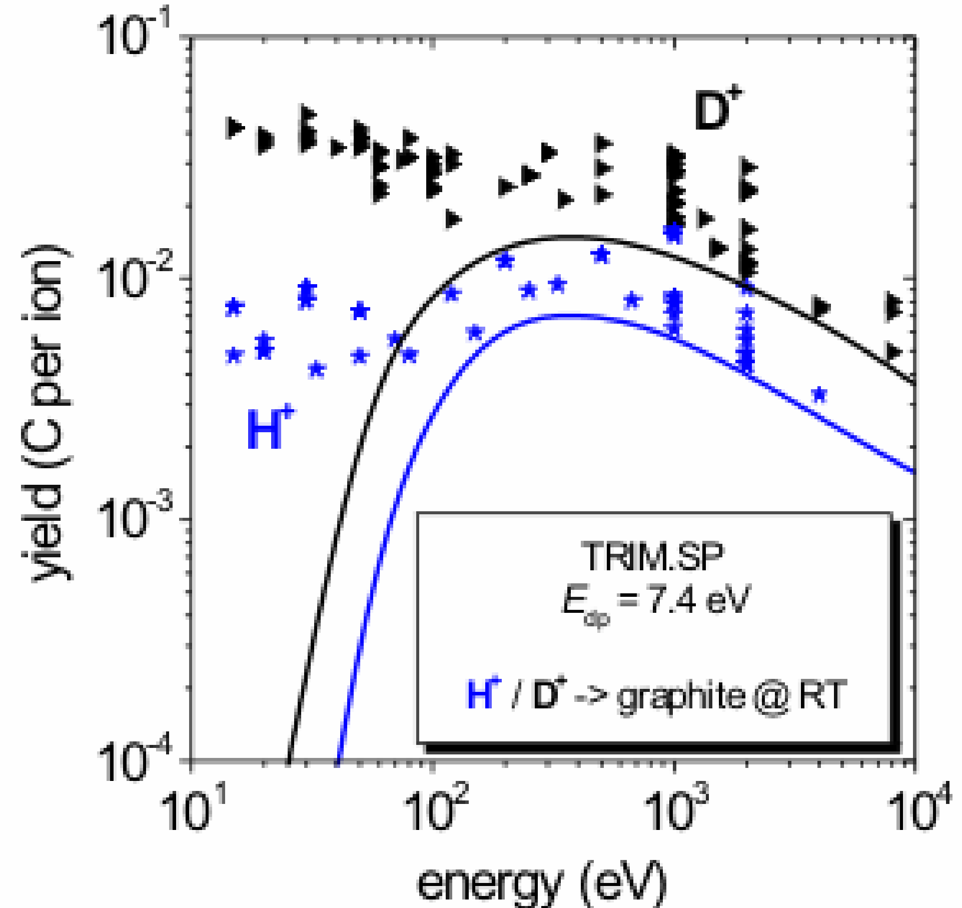
- **Chemical Sputtering** is a process whereby ***ion bombardment causes or allows a chemical reaction to occur*** which produces a particle that is weakly bound to the surface and hence easily desorbs in the gas phase.

erosion of graphite by energetic hydrogen

it is not chemical erosion
H^0 at T > 400 K with a max. at ≈ 650 K – 800 K

it is not physical sputtering
energetic ions $E > E_{th}$,
no chemistry

but its chemical sputtering
hydrogen ions, low-T, low-E



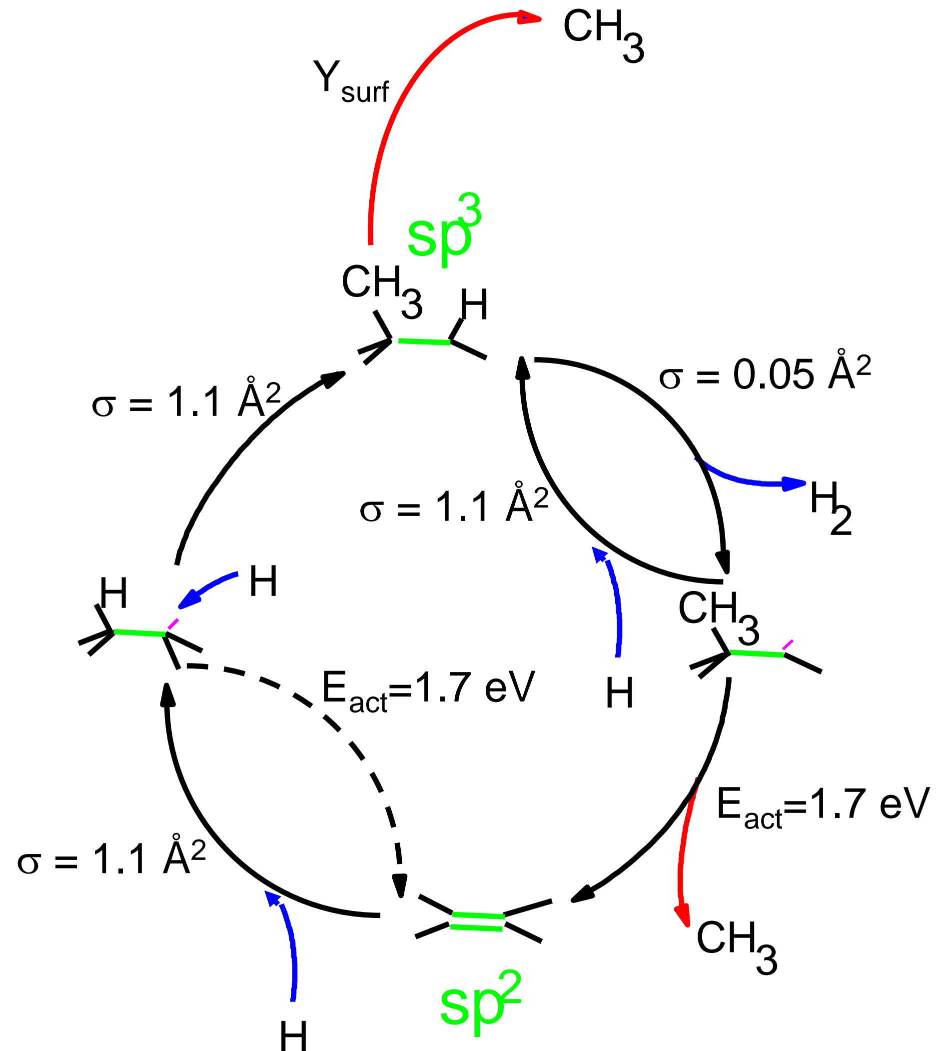
Data: M. Balden and J. Roth, J. Nucl. Mater. 280 (2000) 39–44

Chemical Sputtering: one attempt

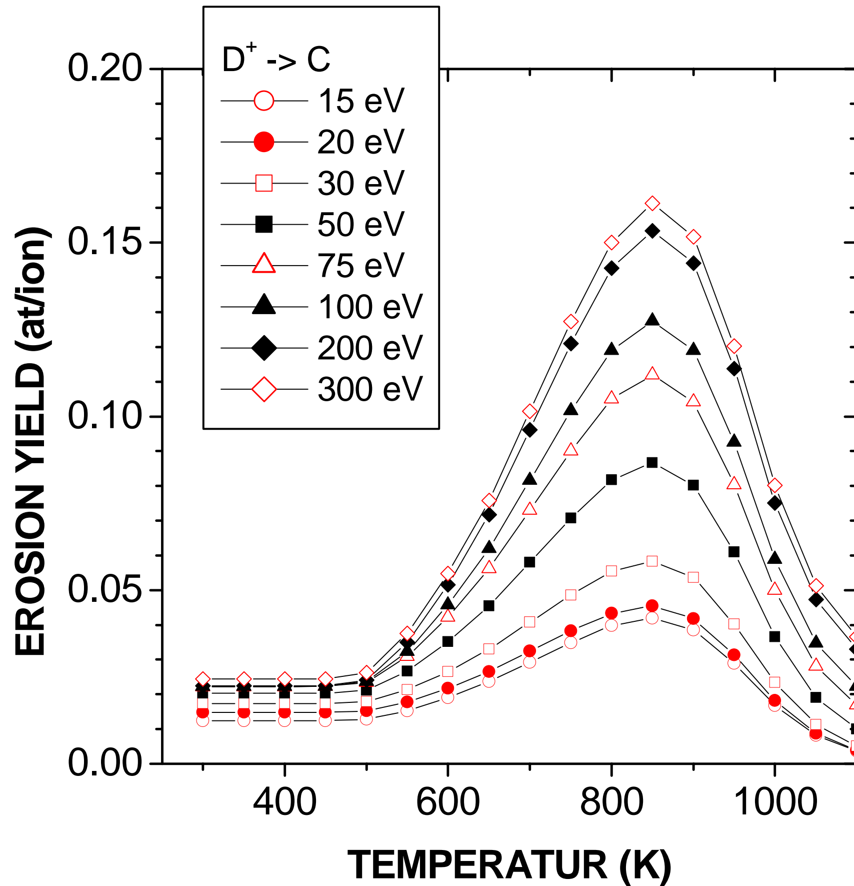
Hydration and erosion circle:

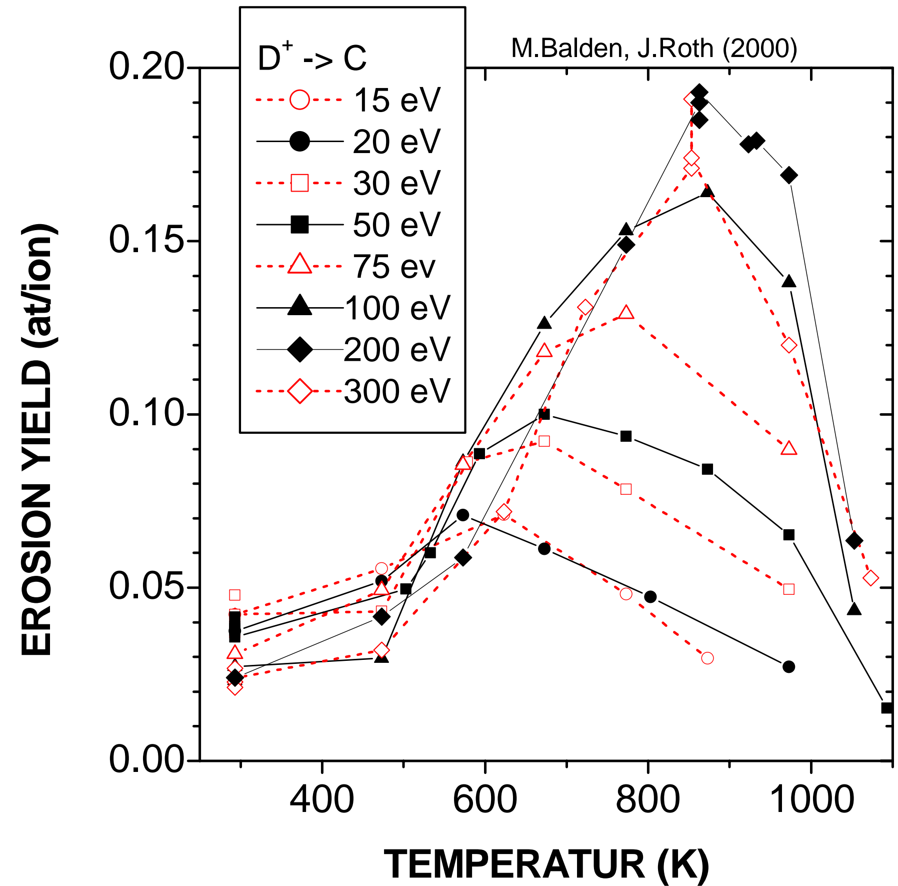
A. Horn et al., Chem. Phys. Lett. 231, 193 (1994)
J. Roth, J.Nuclear Mat. 266-269, 51 (1999)

- Ion induced release of weakly bound hydrocarbon radicals complexes from the surface



Chemical Erosion at elevated temperatures



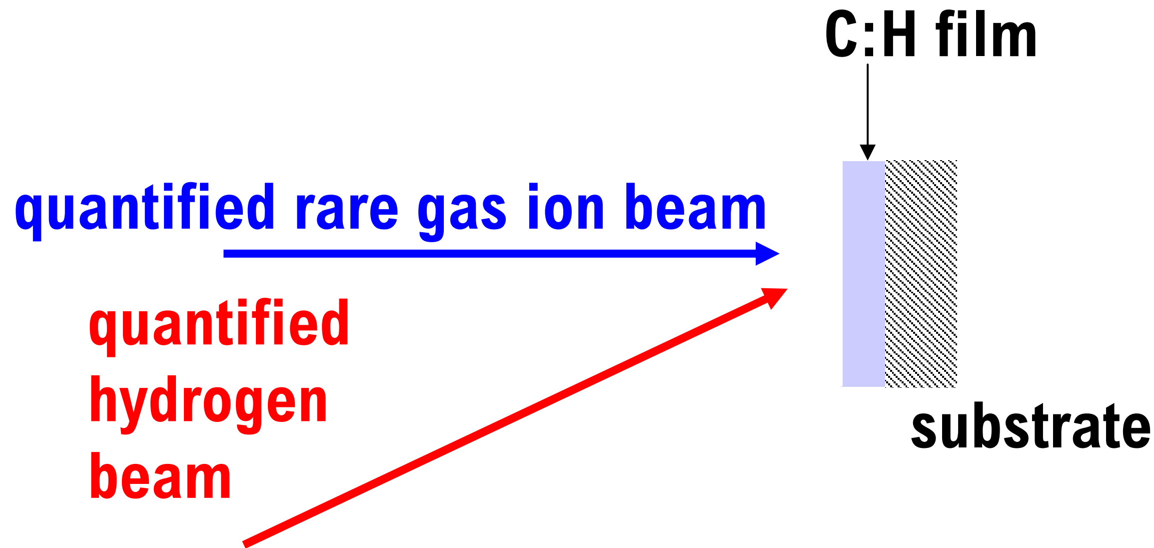


- Adequate modeling of erosion
- does not explain shift oft maximum with energy

IPP

Quantified particle-beam experiments: separating physics from chemistry

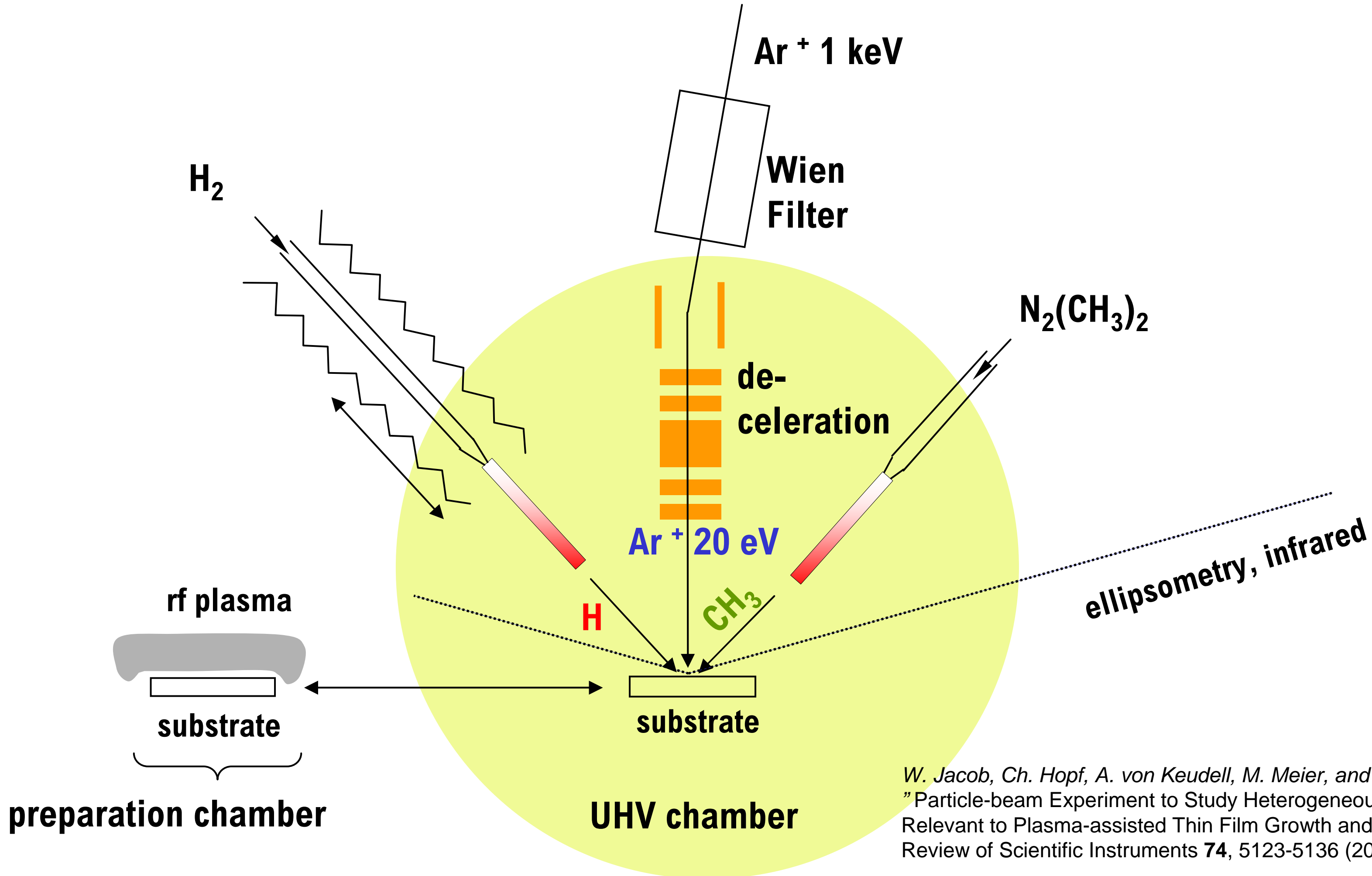
Measuring erosion yields



$$\text{erosion yield} = \frac{\text{measured erosion rate in eroded carbon atoms per cm}^{-2}\text{s}^{-1}}{\text{impinging ion flux per cm}^{-2}\text{s}^{-1}}$$

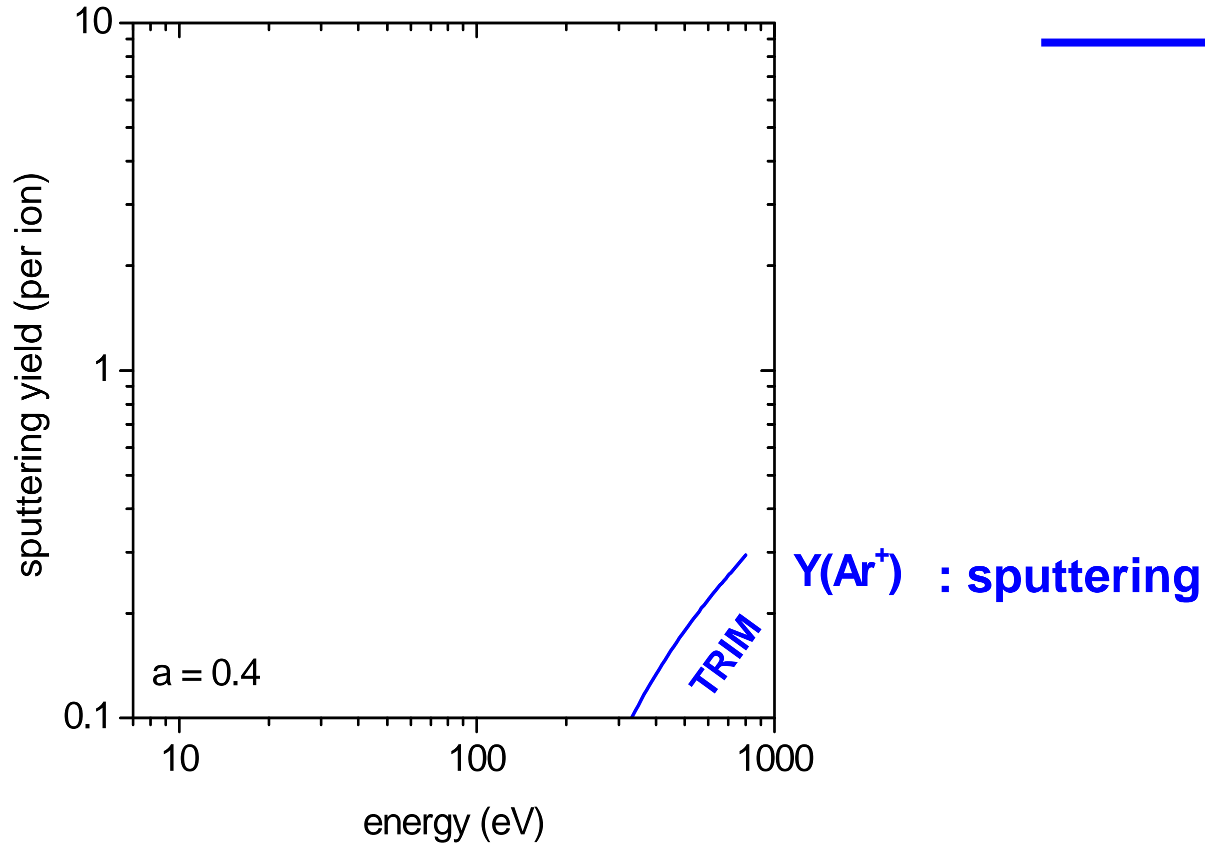
Quantified particle-beam experiments

UHV experiment with 2 radical beam sources and one ion beam source

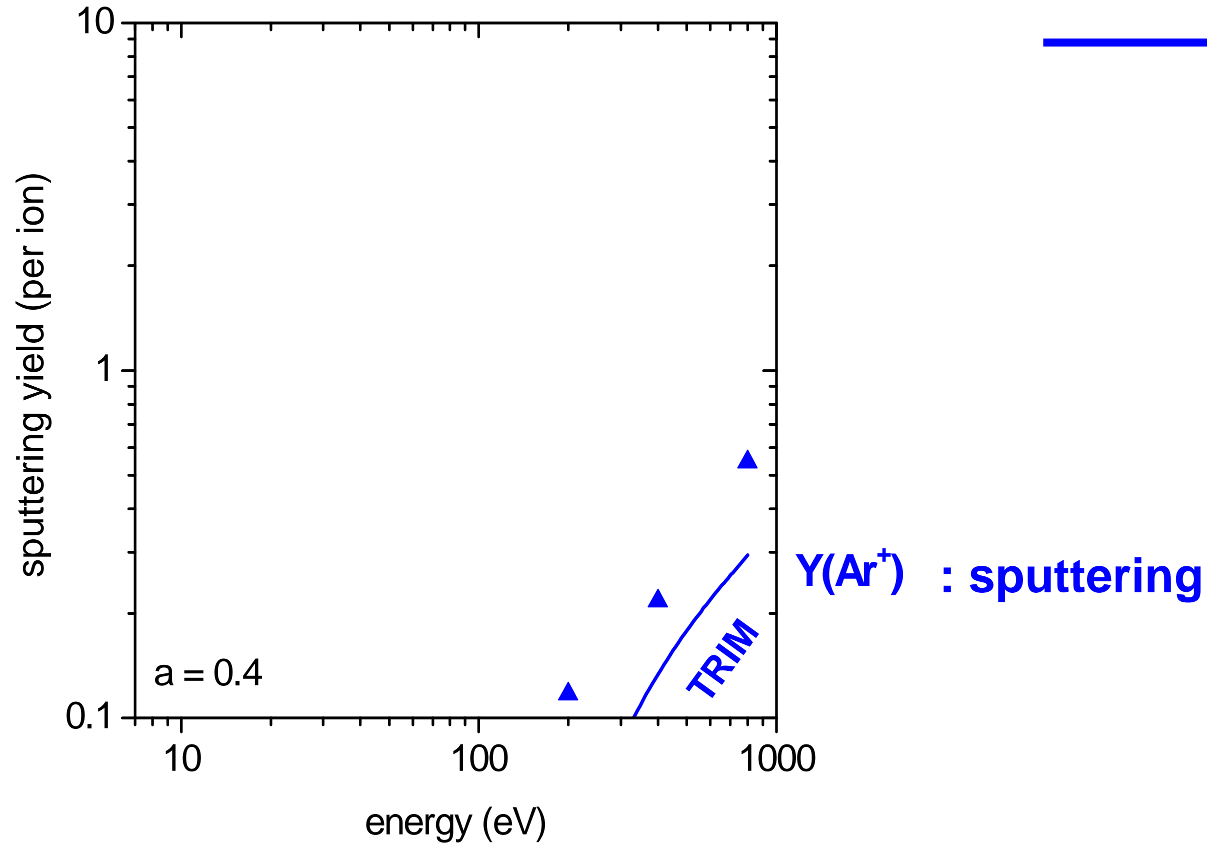


W. Jacob, Ch. Hopf, A. von Keudell, M. Meier, and T. Schwarz-Selinger:
*"*Particle-beam Experiment to Study Heterogeneous Surface Reactions Relevant to Plasma-assisted Thin Film Growth and Etching*"*,
Review of Scientific Instruments **74**, 5123-5136 (2003).

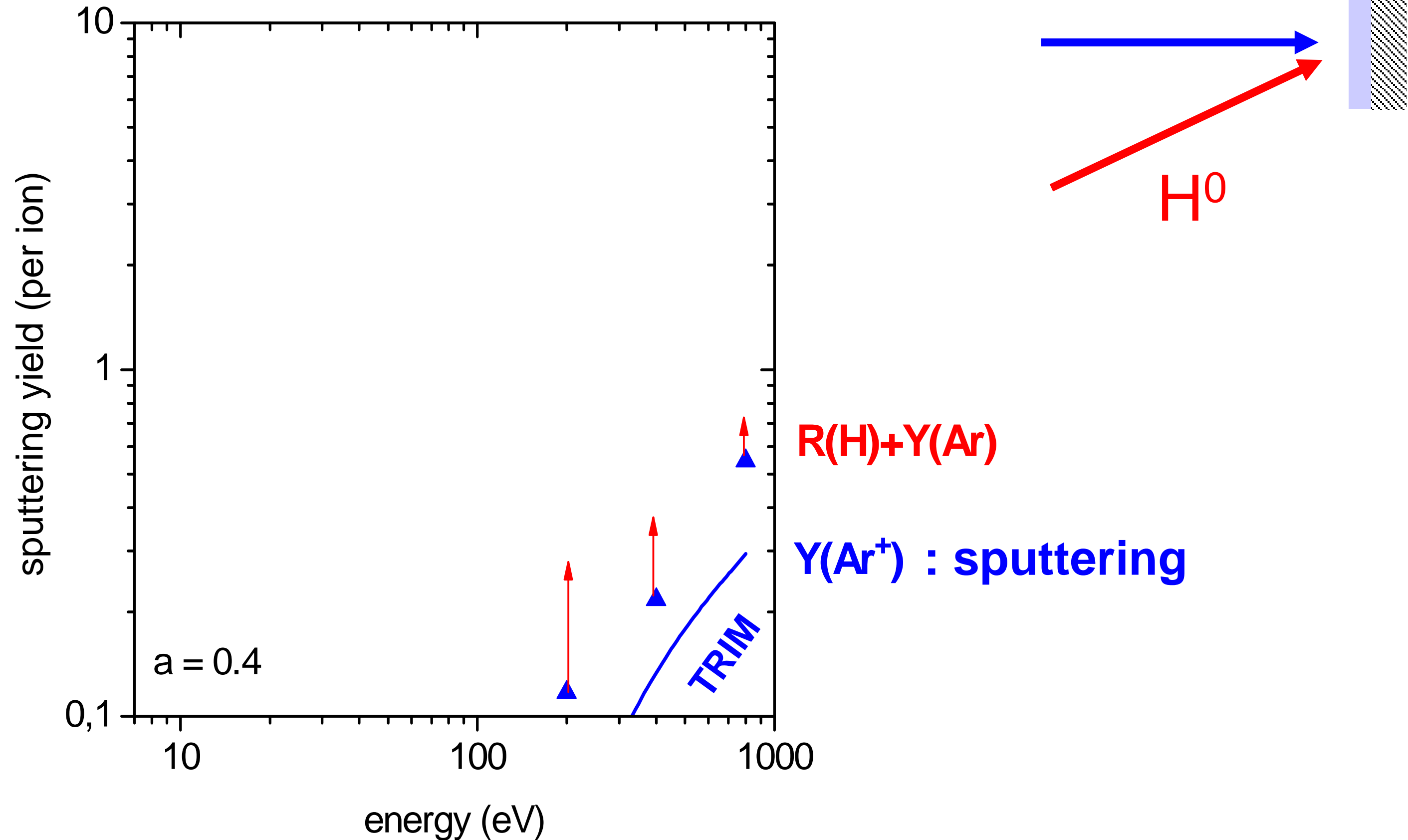
physical sputtering



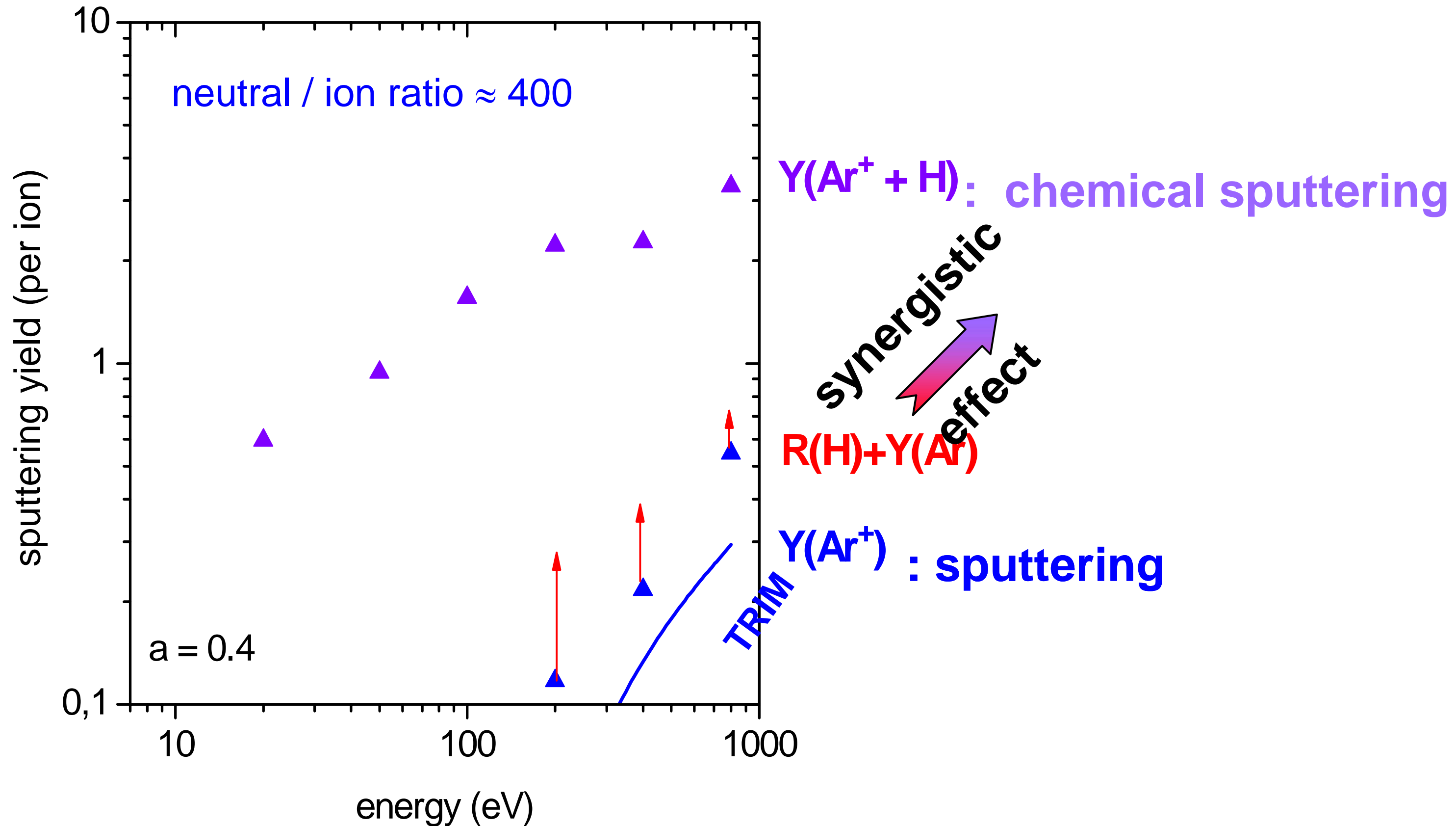
physical sputtering



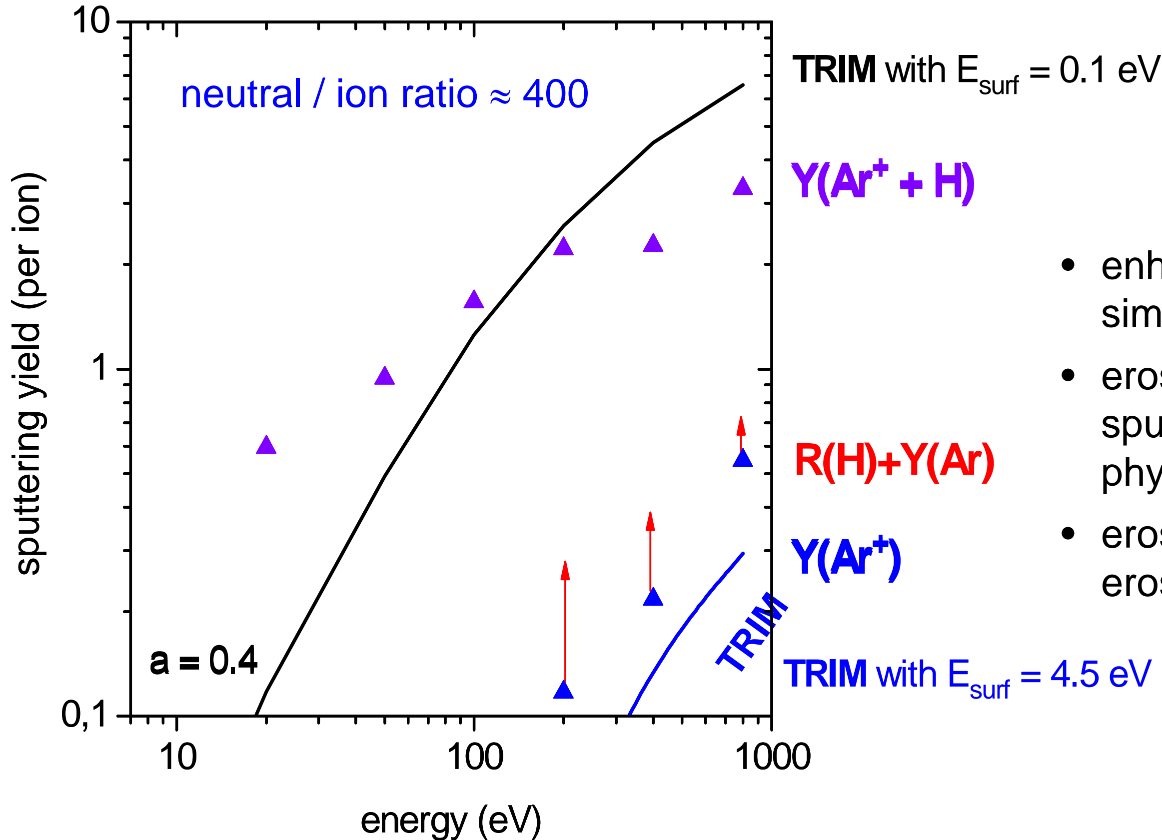
physical sputtering + chemical erosion



physical sputtering + chemical erosion

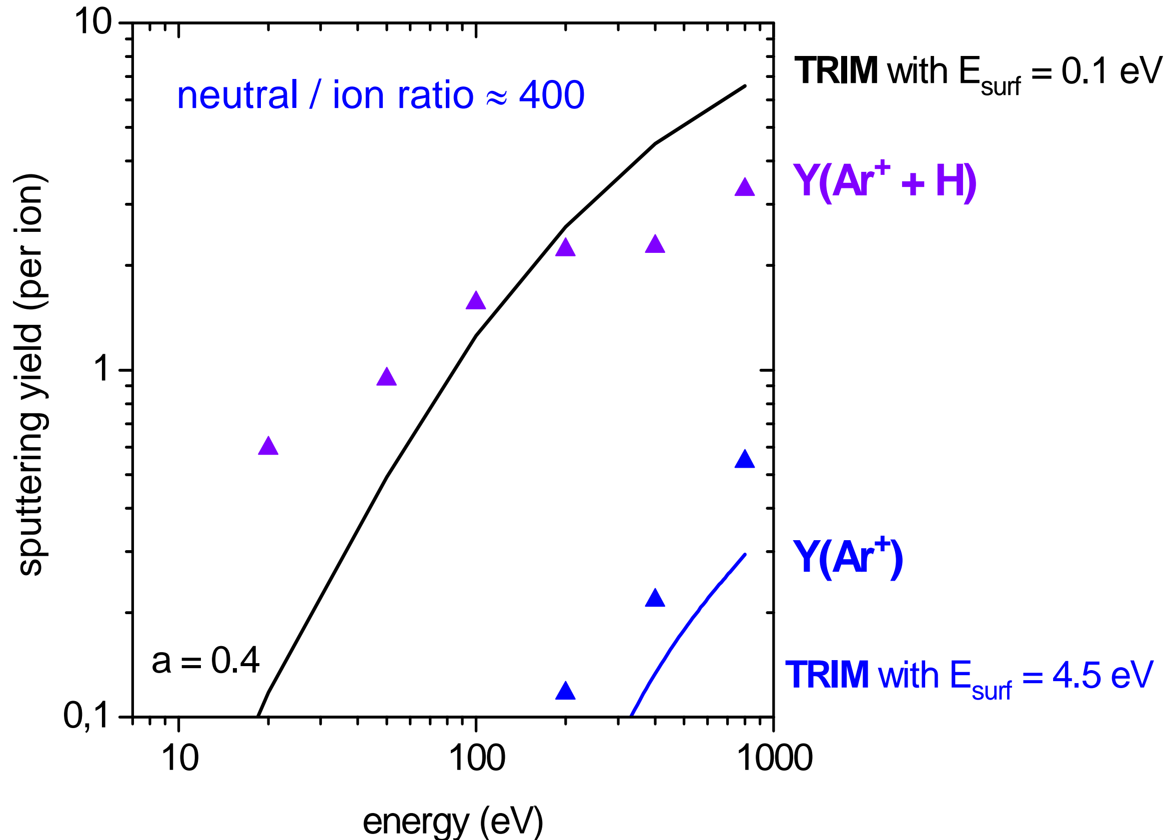


physical sputtering + chemical erosion



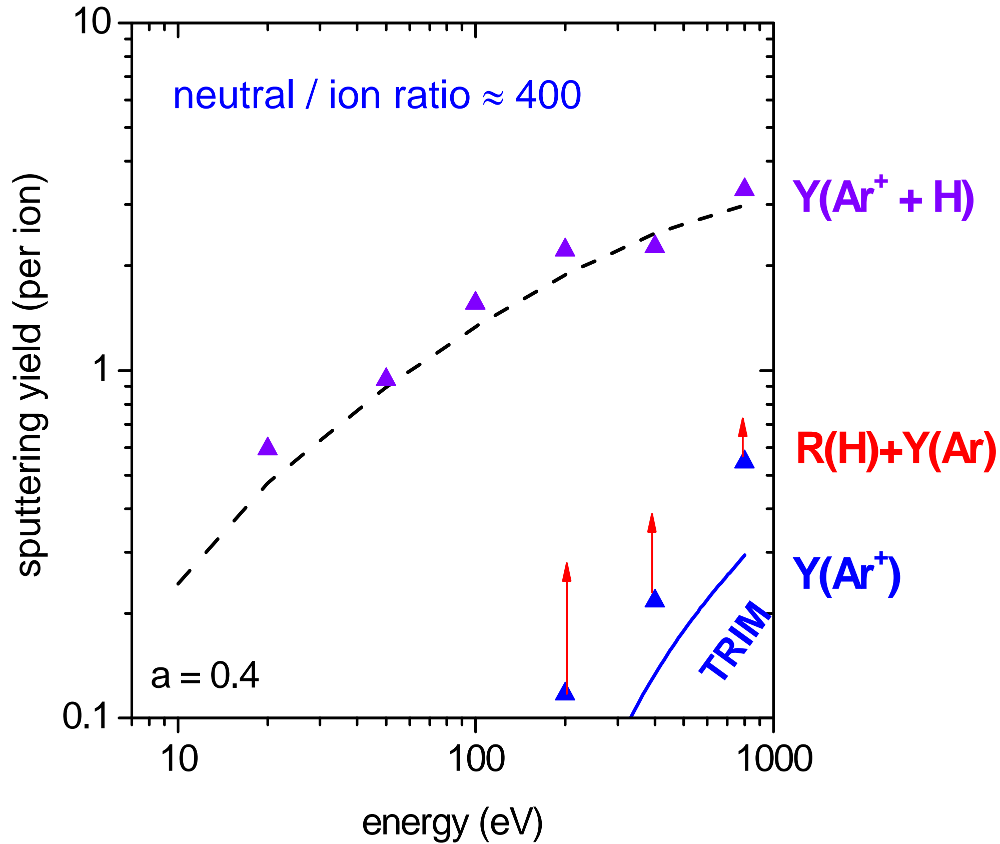
- enhanced erosion above 200 eV for simultaneous interaction
- erosion below threshold for physical sputtering (threshold energy for physical sputtering ≈ 60 eV
- erosion at 20 eV >> pure chemical erosion ⇒ '***chemical sputtering***'

physical sputtering + chemical erosion



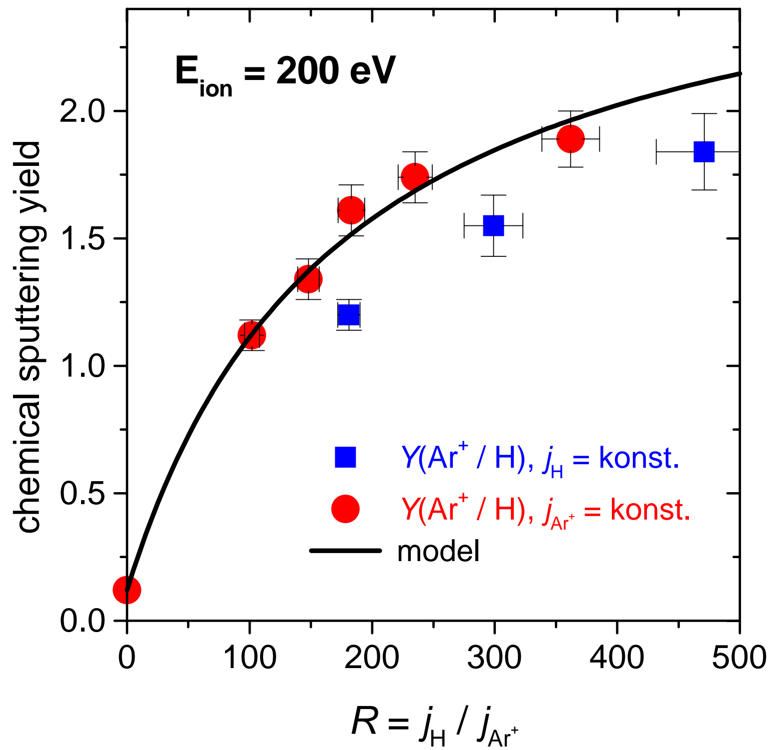
sputtering of weakly bound surface radicals seems not to be physical

chemical sputtering



model for chemical sputtering

$Ar^+|H$ flux dependence



$$Y_{\text{Modell}} = Y_{\text{phys}}(1 - \Theta_{\text{CH}}) + Y_{\text{chem}}\Theta_{\text{CH}}$$

$$n_0 \frac{d\Theta_{\text{CH}}}{dt} = j_{\text{H}}(1 - \Theta_{\text{CH}}) p^{\text{H}}_{\text{Einbau}} - j_{\text{Ion}}\Theta_{\text{CH}} p^{\text{H}}_{\text{Freisetzung}}$$

Mit $R = j_{\text{H}}/j_{\text{Ion}}$ und $S = p^{\text{H}}_{\text{Freisetzung}}/p^{\text{H}}_{\text{Einbau}}$

$$\boxed{Y_{\text{Modell}} = Y_{\text{phys}} + \frac{R}{R+S}(Y_{\text{chem}} - Y_{\text{phys}})}$$

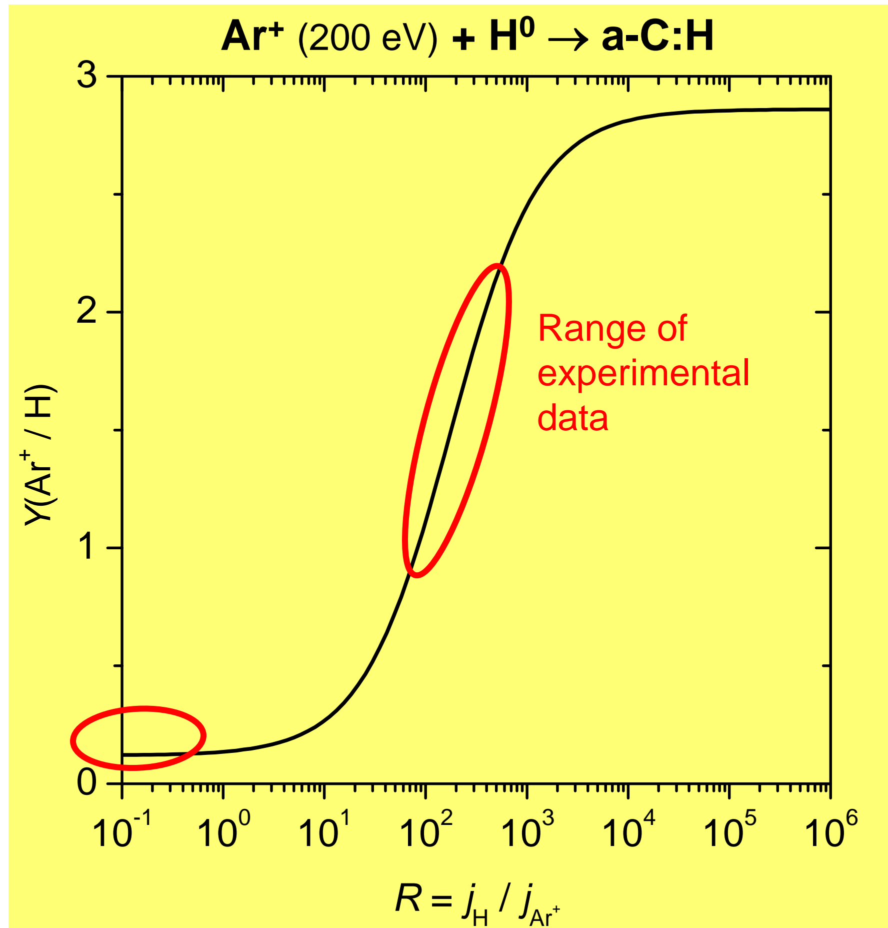
Fit parameters:

$S = 176$

$Y_{chem} = 2.86$

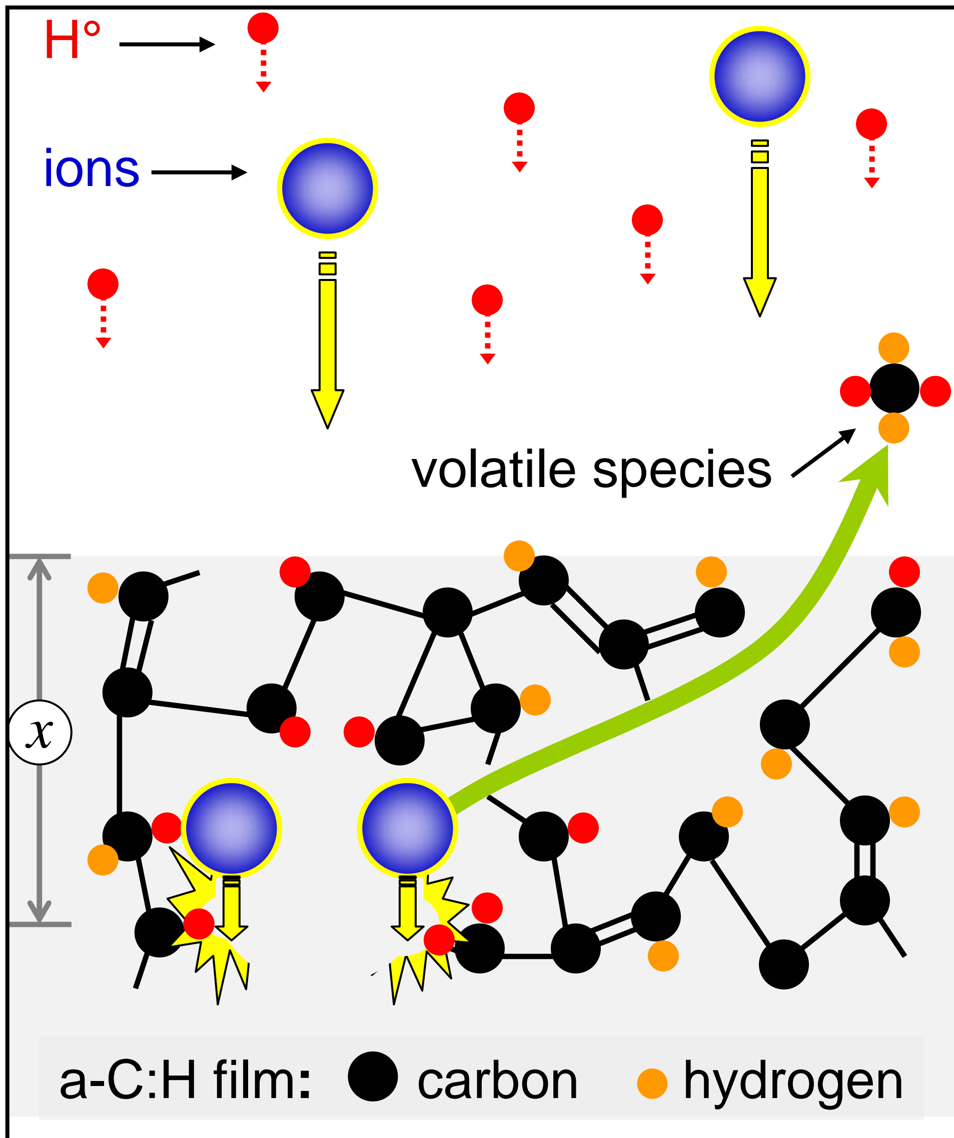
$Y_{phys} = 0.12$

Ar^+|H flux dependence



Saturation requires much more H than ions (R > 1000)

Chemical sputtering mechanism



1. ions break C–C bonds

2. H° passivates broken bonds

Repetition of 1 and 2

➔

3. volatile hydrocarbons

diffusion to the surface

desorption

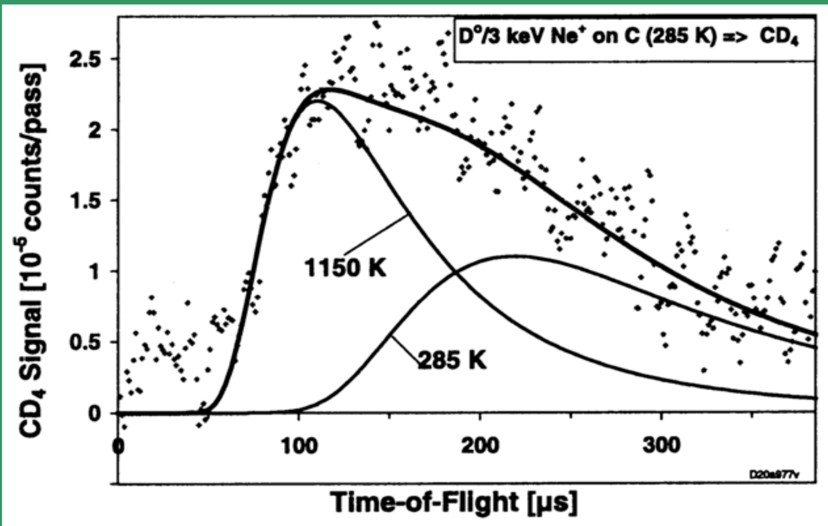
Supporting results from literature

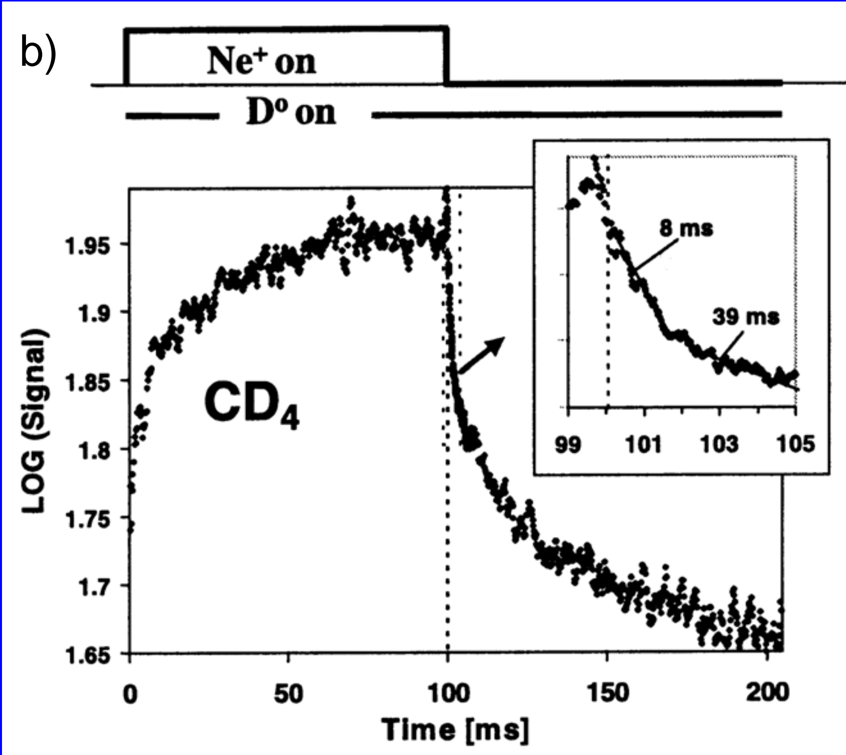
1. CH_4 main (C_1-) erosion product (Vietzke et al. J. Nucl. Mater. 128&129, 545 (1984))

2. energy distribution of erosions products

3. time delay between end of ion bombardment and end of particle release

from E. Vietzke, J. Nucl. Mater 290, 158 (2001)





Chemical sputtering model

$$Y(ions \mid H) \propto \int y_{bb}(x) \cdot p_{pass}(x) dx$$

bond breaking due to ion impact

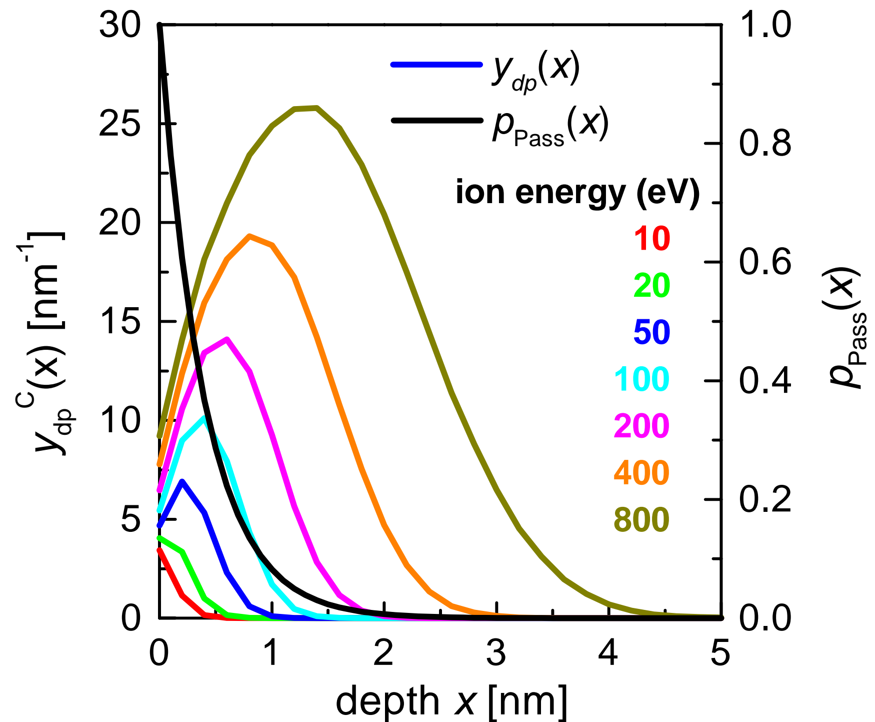
passivation by atomic H

$$Y(ions \mid H) = a \cdot \int y_{dp}(x) \cdot e^{(-x/\lambda)} dx$$

displacement events per depth interval calculated by TRIM.SP

exponential decay, maximum range about 2 nm, known from plasma experiments

a is a fit parameter



E_{dp}^{C} = 5 eV, λ = 0.4 nm

Energy dependence

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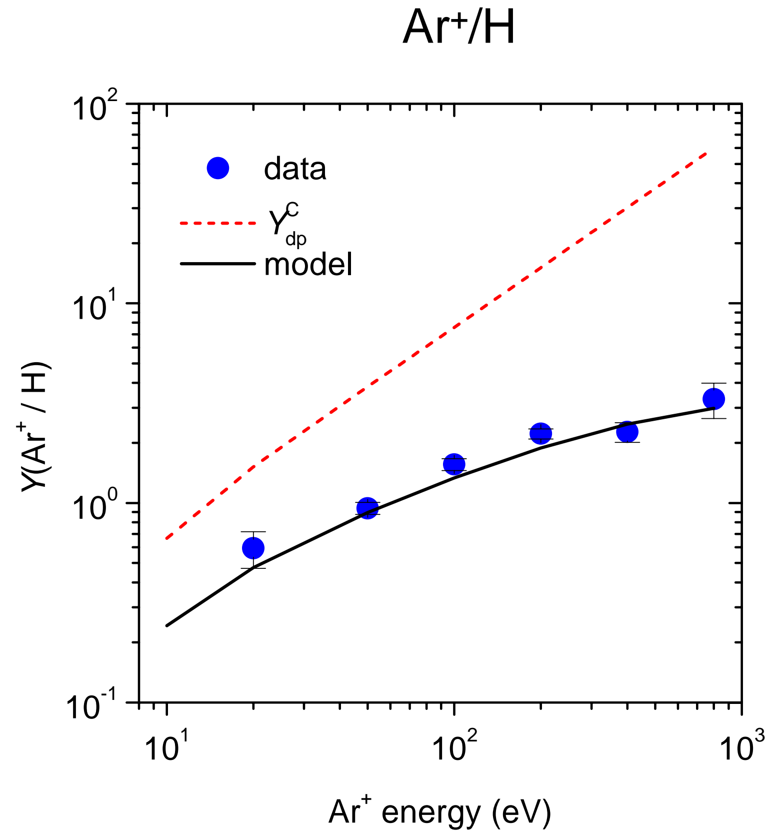
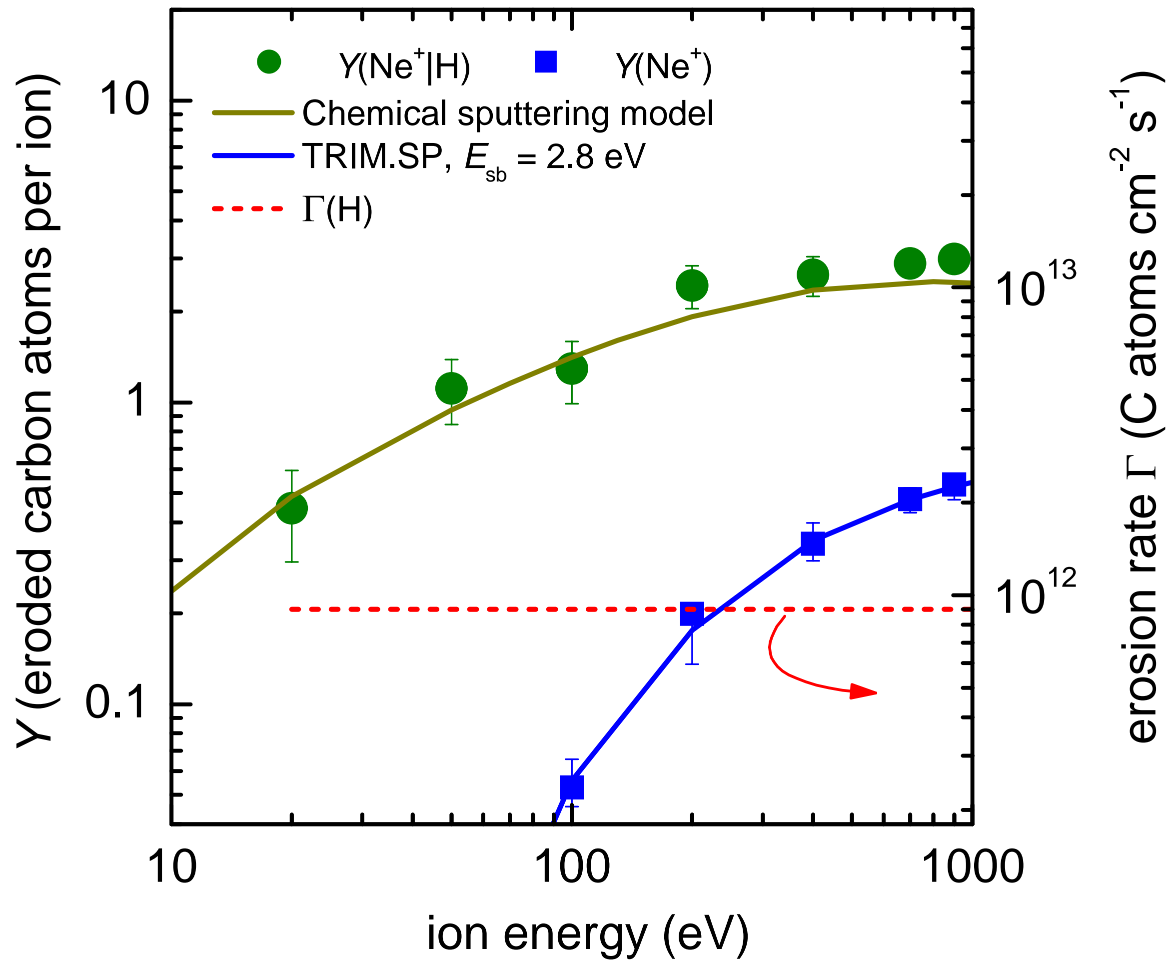


$a = 0.4$

$j_H = 1.4\times10^{15}$ cm^{-2} s^{-1}, $j_{Ar+} = 3.6\times10^{12}$ cm^{-2} s^{-1}, $R = j_{H/} j_{Ar} \approx 400$

: Ne^+ + H



- Excellent agreement between model and data (same parameters as for Ar, i.e., a = 0.4))
- yield > 1 for E_{ion} >50 eV

Energy dependence: Modeling results

0.8
0.6
0.4
0.2
0.0

chemical sputtering yield

H^0 +

He^+
T^+
D^+
H^+

10
100
1000

ion energy (eV)

a = 0.4
R ≈ 400

Energy dependence: Modeling results

chemical sputtering yield (per ion)

10

1

0.1

0.01

N_2^+

Ar^+

Ne^+

He^+

H_2^+

10 100 1000

energy (eV)

a = 0.4

R ≈ 400

Nitrogen puffing into the divertor

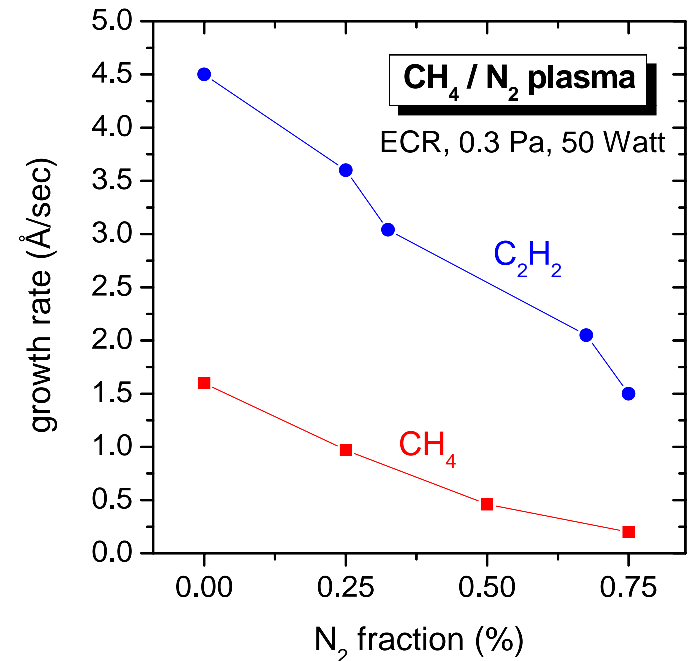
Idea: (by F.L. Tabarés et al., Plasma Phys. Control. Fusion 44, L37-42 (2002))

Nitrogen acts as scavenger for reactive carbon radicals thereby reducing redeposition.

Based on:
laboratory experiments that show reduced growth rate in hydrocarbon plasmas when nitrogen is added.

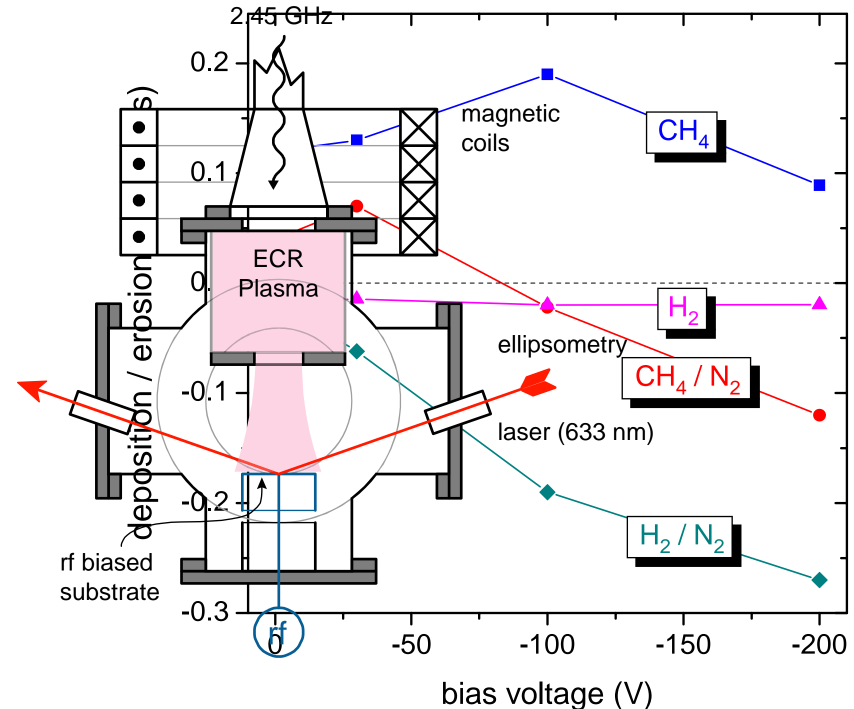
➲ Any direct proof for a scavenger effect?

➲ what about surface effects?



Nitrogen puffing into the divertor

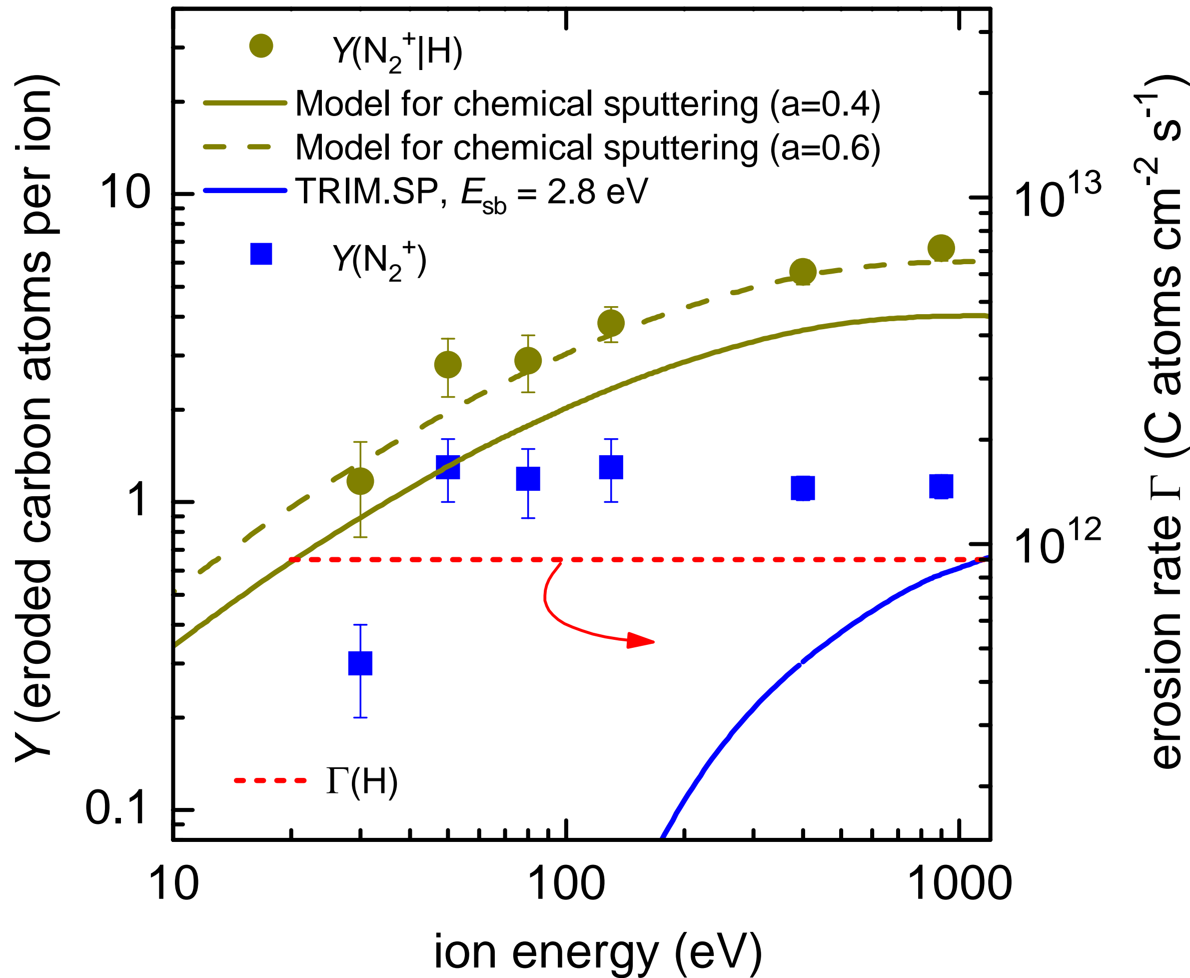
experiments in a well defined remote ECR plasma show:



➲ changeover from deposition to erosion for CH_4 / N_2 plasmas at higher ion energies can only be explained by surface effects (the gas phase chemistry remains unchanged!)

➲ chemical sputtering

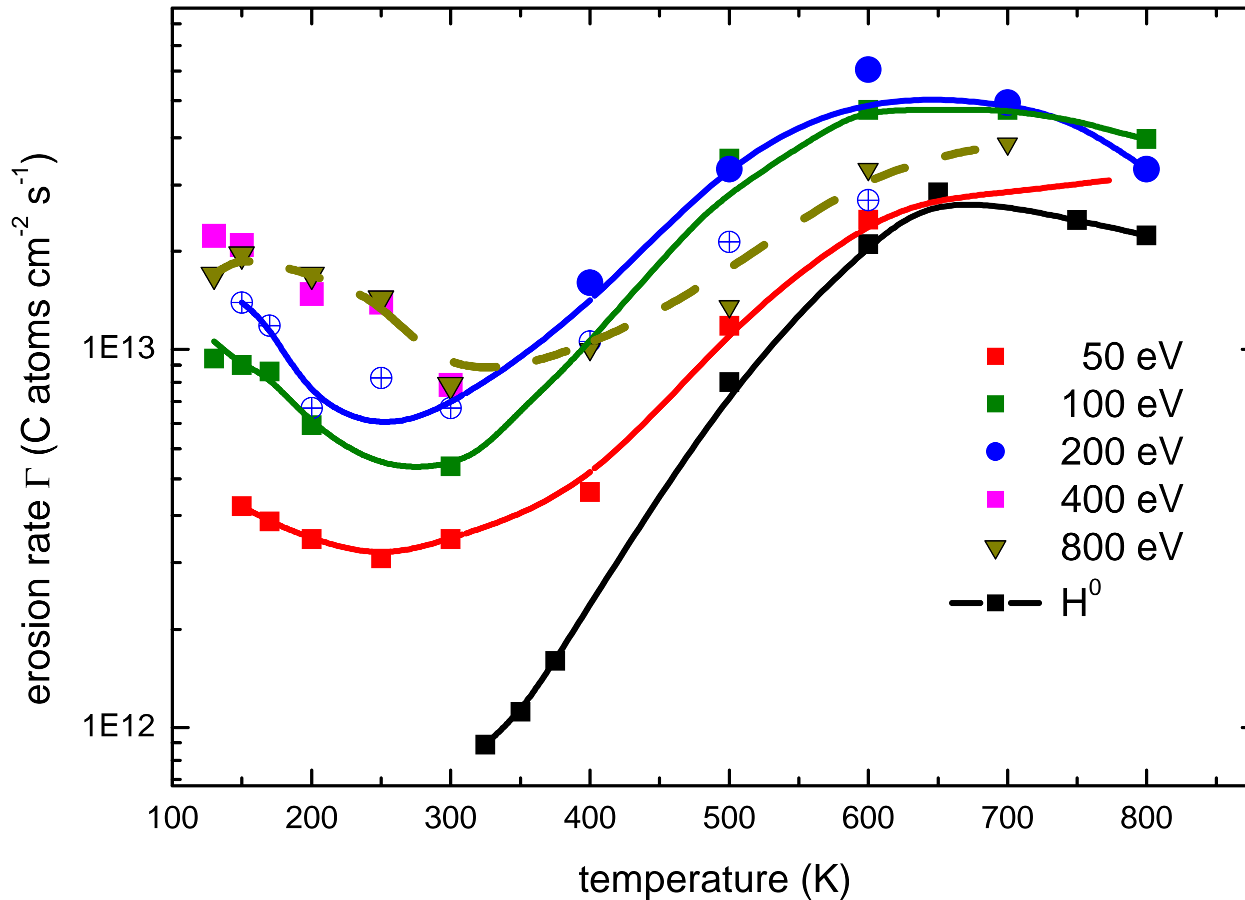
Chemical sputtering: N_2^+ + H



- Good fit of the energy dependence, but only for a = 0.6 (instead of 0.4)
- yield ≤ 1 in whole range
- highest chem. Sputt. yield of all investigates species *(good mass match to C, two atoms per ion, chemical activity)*

Ar + H: temperature dependence

IPP



M. Schlüter et al. 2006

300 to 800 K

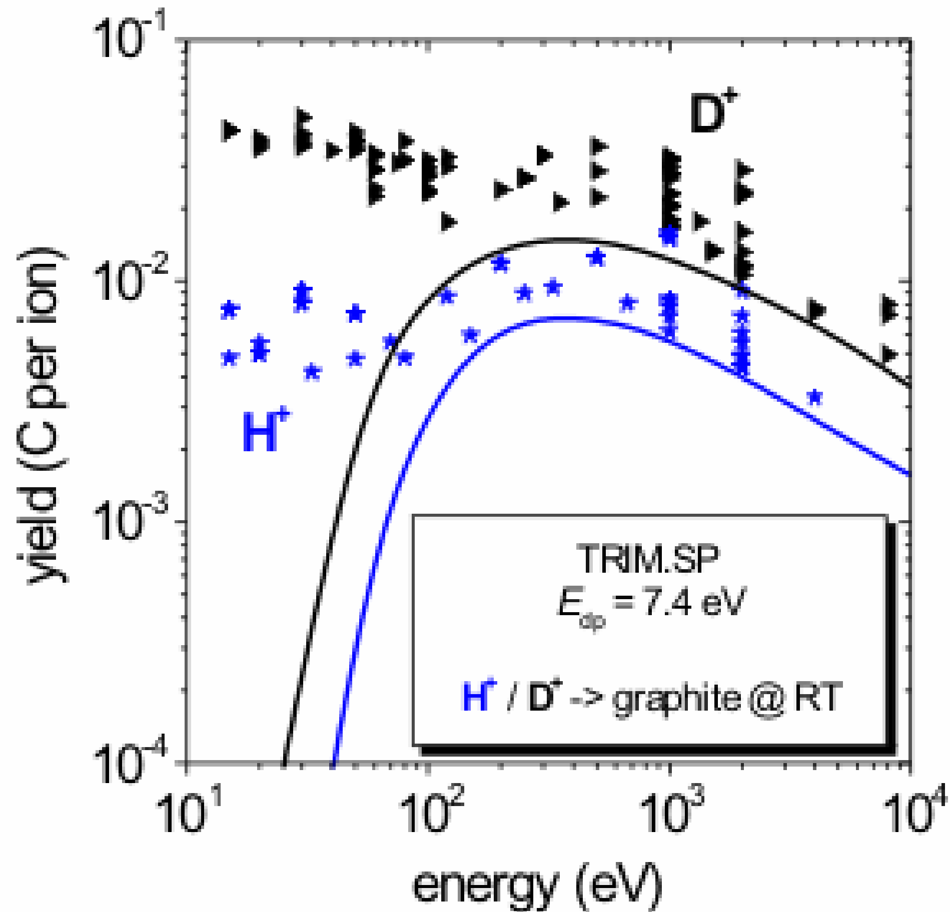
- increase with T
- increase with E_{ion}
- at 800 eV rates for T>400 K lower

300 to 120 K

- increase with **decreasing** T
- increase with E_{ion}
- minimum around 250 to 300 K

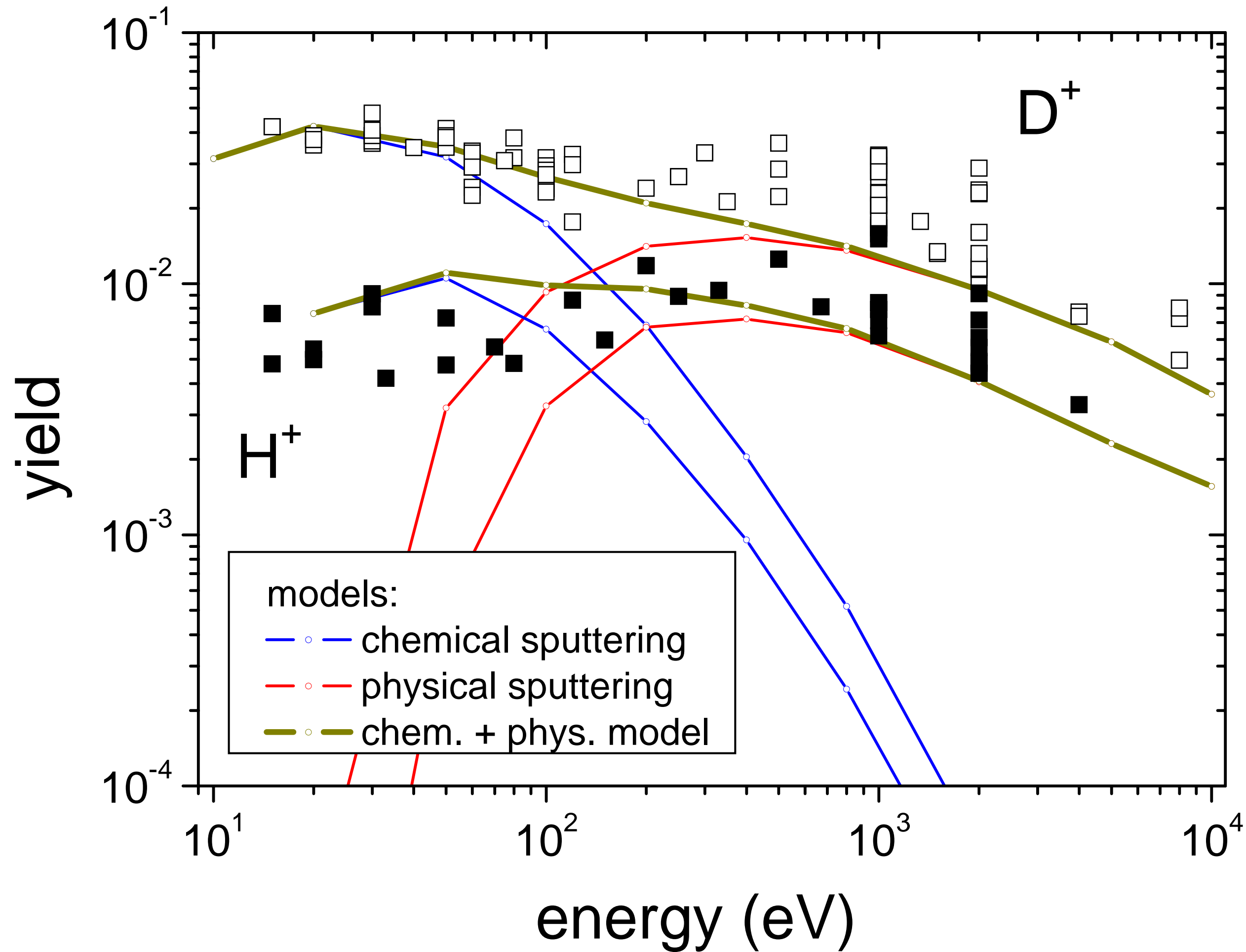
R ≈ 400

erosion of graphite by energetic hydrogen



Chemical sputtering with reactive ions

IPP



C. Hopf and W. Jacob 2005

Chemical sputtering with reactive ions

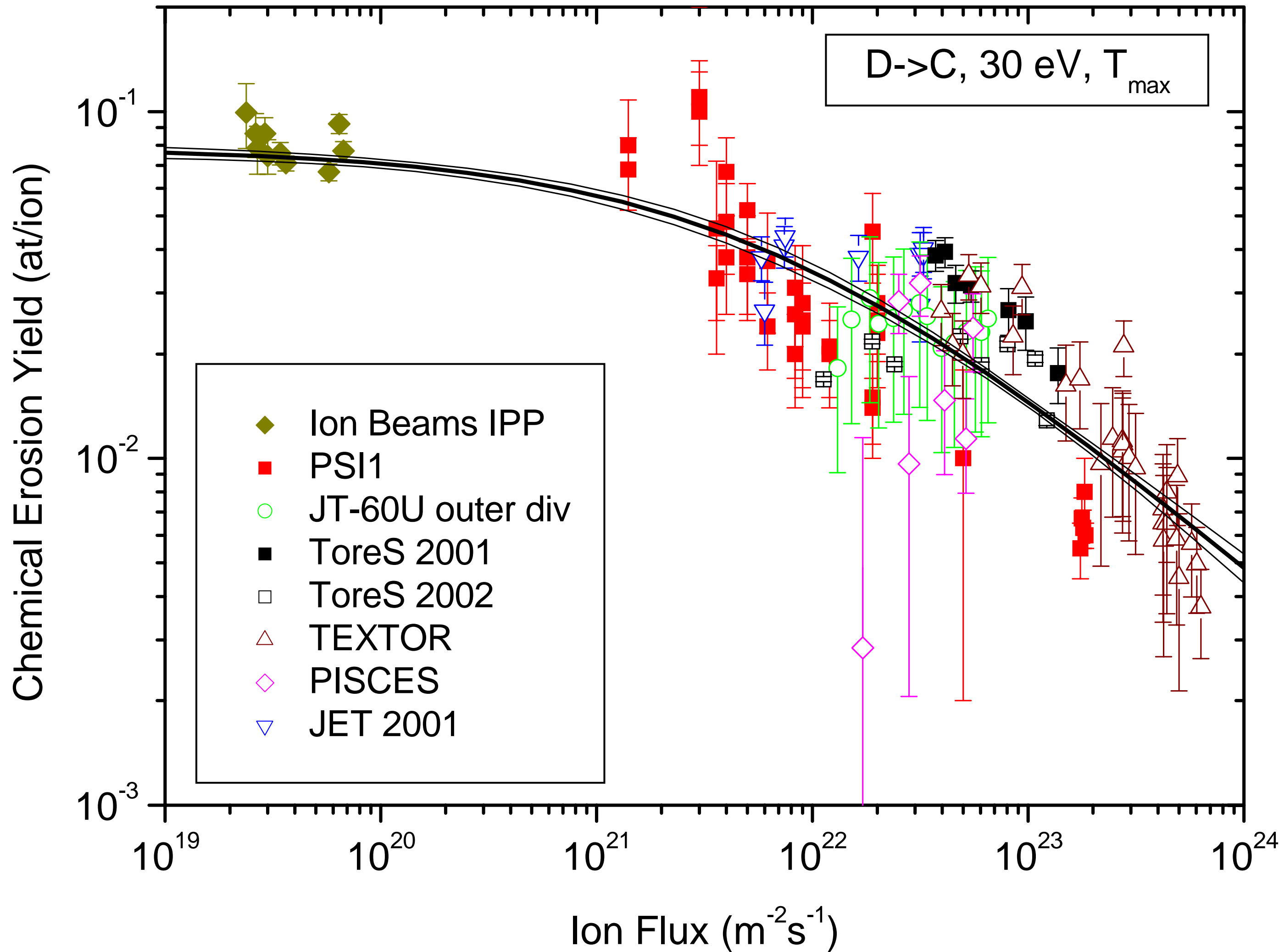
total yield = chemical sputtering + physical sputtering

$$Y(E) = \int y_{\mathrm{dp}}^{\mathrm{C}}(x,E)\, n(x,E) \exp(-x/\lambda)\, \mathrm{d}x + Y_{\mathrm{phys}}(E)$$

$Y_{\mathrm{phys}}(E)$	phys. sputtering yield	TRIM.SP
$y_{\mathrm{dp}}{}^{\mathrm{C}}(x,E)$	ion induced damage	$E_{\mathrm{sb}}{}^{\mathrm{C}}$ = 7.4 eV $E_{\mathrm{dp}}{}^{\mathrm{C}}$ = 5.0 eV
$n(x,E)$	implanted hydrogen	

$\exp(-x/\lambda)$	depth dependent probability for outdiffusion of erosion products	λ = 0.4 nm

Erosion (Chemical sputtering) at high ion fluxes

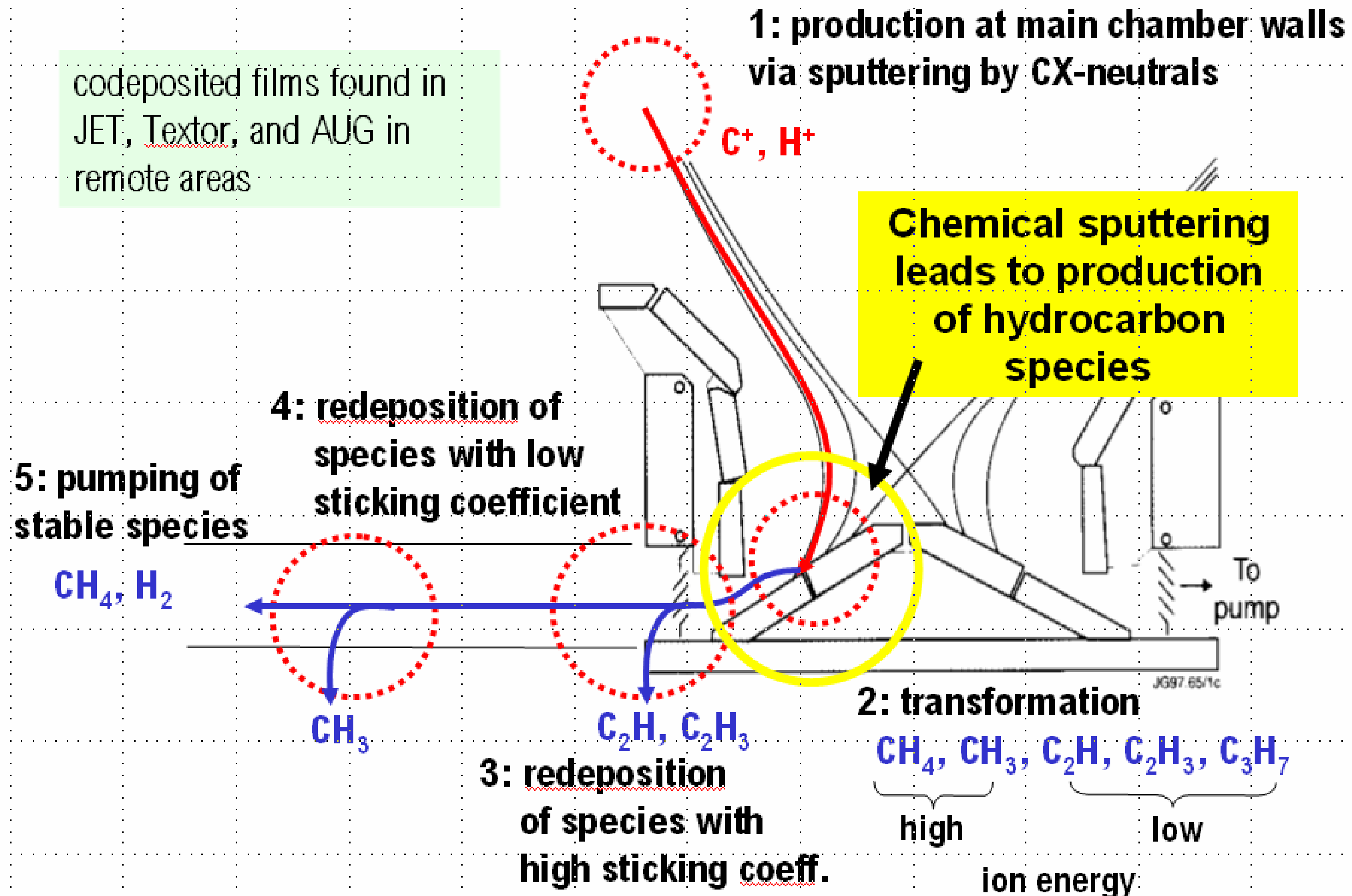


Fitting formula:

$Y = Y_{low}/(1+(\Gamma/\Gamma_0)^{\varepsilon})$

Results from fitting: $Y_{Tmax}(\Gamma) = 0.79/(1+(\Gamma/6x10^{21})^{0.54})$

film growth / codeposition



Plasma-surface interactions in general

A large variety of species impinges on the surface

Classes of species:	General assumption
stable neutrals (mostly working gas)	⇒ non reactive
neutral radicals	⇒ reactive, sticking at surface ***"What is the sticking coefficient?"***
ions	⇒ stick, enhance sticking of radicals modify deposited material

All these species show mutual interactions!

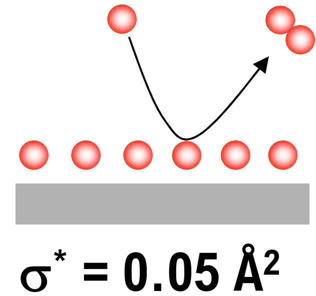
Radical/radical interaction — little is known, example: **CH_3 | H synergism**

Ion/radical interaction

ion/CH_3	"ion-induced stitching" postulated in literature **ion-induced sticking**
ion/H	ion-induced etching (reactive ion etching, RIE) **chemical sputtering**

Interaction of H^0 with a-C:H

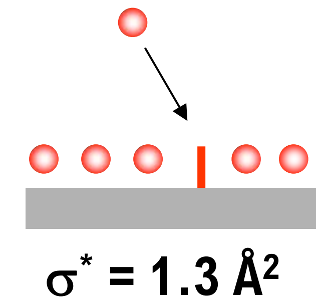
Abstraktion



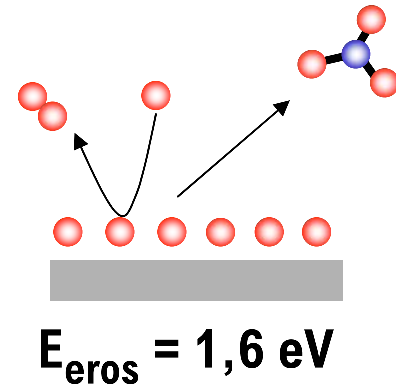
in equilibrium

≈5% active surface sites!

Addition

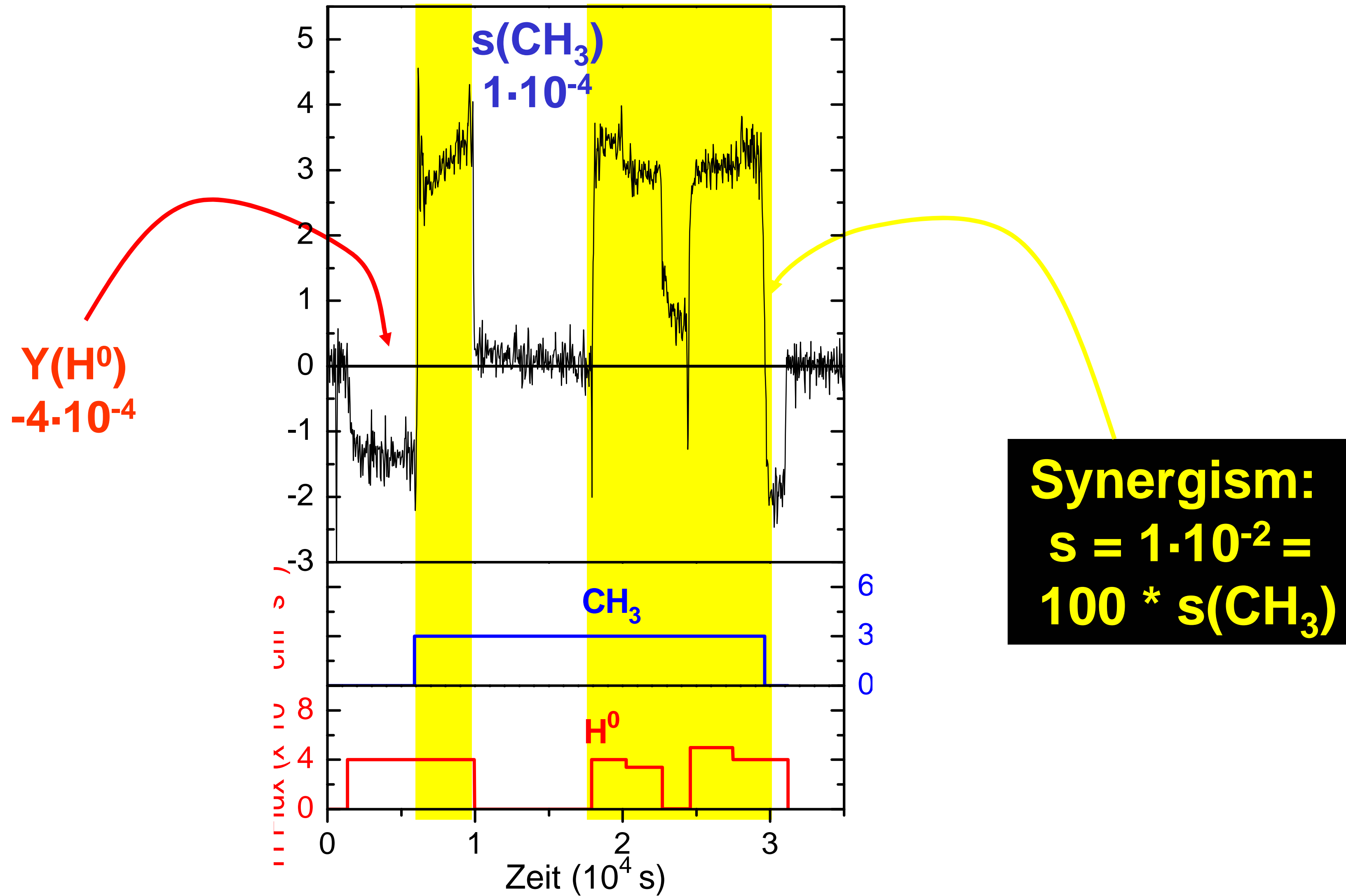


thermisch aktivierte Erosion



⇒ J. Küppers, Surf. Sci. Rep. 22, 249 (1995)

Interaction of H^0 and CH_3 with a-C:H



Summary

- **Physical sputtering:** for the most part well understood
  - well modeled by TRIM.SP (binary collision approximation)
  - energy, projectile mass, angle, roughness
- **Chemical erosion:** for the most part well understood
  - thermally activated process
  - can be influenced by doping

- ***Chemical sputtering**:* increase of yield and lowering of threshold
- mechanistic model for *chemical sputtering*
- flux ratio dependence (rate equation model): high H fluxes required
- energy dependence: bond breaking × passivation
- predictions for other ions, e.g. H, D, T, He, N_2, ..
- temperature dependence of the erosion maximum not understood
- decrease in erosion rate at high fluxes not under stood

Exercises

IPP

1) Calculate first wall or divertor plate erosion based on chemical sputtering
For example, assume the following conditions:

	T_{surf}(K)	E_0 (eV)	flux Γ ($m^{-2}s^{-1}$)
Divertor	700	30	10^{23}
First wall	500	200	10^{20}

Comparison can be made with physical sputtering to see which process dominates under which conditions. What might be the implication of having an all-carbon ITER?

2) Try to describe schematically the depth distribution of D in a 500 μm W foil

- for the case of purely diffusion limited release. What would be the ratio of the re-emitted flux to the permeating flux in steady state assuming an ion range of 50 nm.
- for the case of strongly recombination limited surface facing the plasma.
- What would be the optimum position of a diffusion barrier to limit the T inventory inside the first wall