

Chemical Sputtering

von Kohlenstoff durch Wasserstoff

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Content:

- Definitions: Chemical erosion, physical sputtering, chemical sputtering
- Physical sputtering
- Chemical erosion
- Chemical sputtering
- The MAJESTIX experiment: Ion-H interaction: *Chemical Sputtering*
- Summary

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: **CH₃ | H synergism**

Ion/radical interaction

ion/CH₃

“ion-induced stitching” postulated in literature
ion-induced sticking

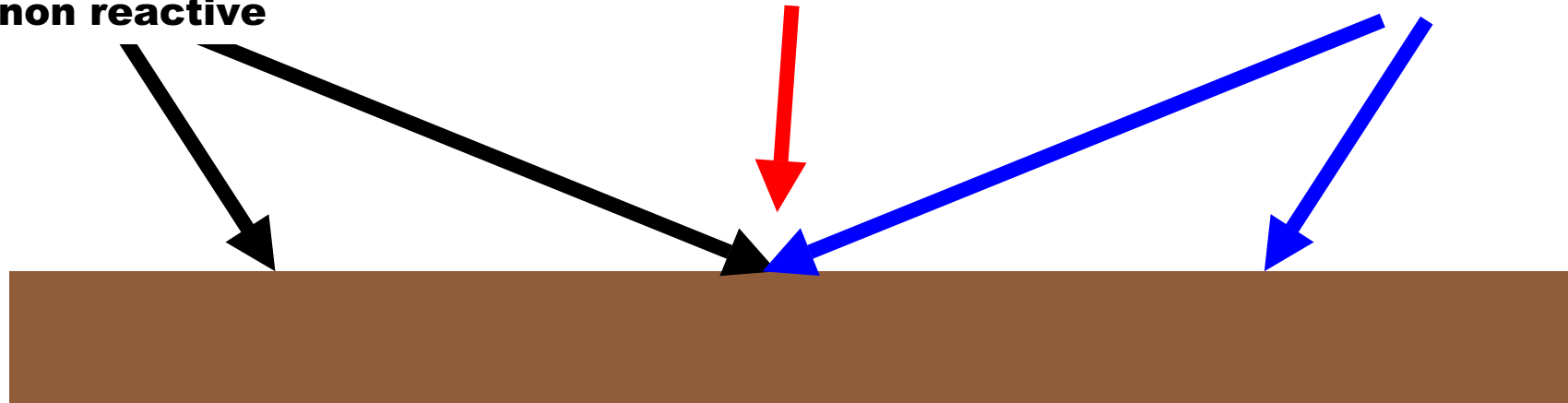
ion/H

ion-induced etching (reactive ion etching, RIE)
chemical sputtering

**ions or energetic neutrals
non reactive**

reactive ions

H atoms



Physical sputtering

- threshold energy
- energy dependence (TRIM.SP)
- isotope effect (kinematic factor)
- no significant T dependence
- all species (incl. inert gases)

Chemical sputtering

- ions + neutrals
- energy dependence
- T dependence
- very low threshold energy
- isotope effect
- ion-to-neutral ratio dep.
- high erosion yield

Chemical erosion

- thermally activated (no threshold energy)
- no isotope effect
- requires chemically reactive species

Chemical sputtering:

- strong variation with surface T
- eroded species = molecules involving atoms of target and projectiles
- no (?) or very low threshold energy
- highly selective (depends sensitively on target projectile combination)
- activation or inhibition possible

Physical sputtering:

- T independent (more or less, for C measurable effect at high T)
- eroded species = atoms or small clusters of target material
- high (>10 - >100 eV) threshold energy (M_1, M_2, E_{SB})
- depends on energy transfer only ($T_{max} = 4 M_1 M_2 / (M_1 + M_2)^2$)

Energy distribution of emitted species:

$$E_{\text{mean}} \approx kT_{\text{surface}}$$

$$E_{\text{mean}} \approx \text{some eV}$$

- well understood (for the most part)
- key parameter is the surface binding energy E_{SB} (= 7.4 eV for carbon)
- depends on energy →
- depends on projectile mass →
- only weakly T dependent
- threshold energy depends on target/projectile combination
- depends on angle of incidence
- depends on substrate material
- depends on target roughness

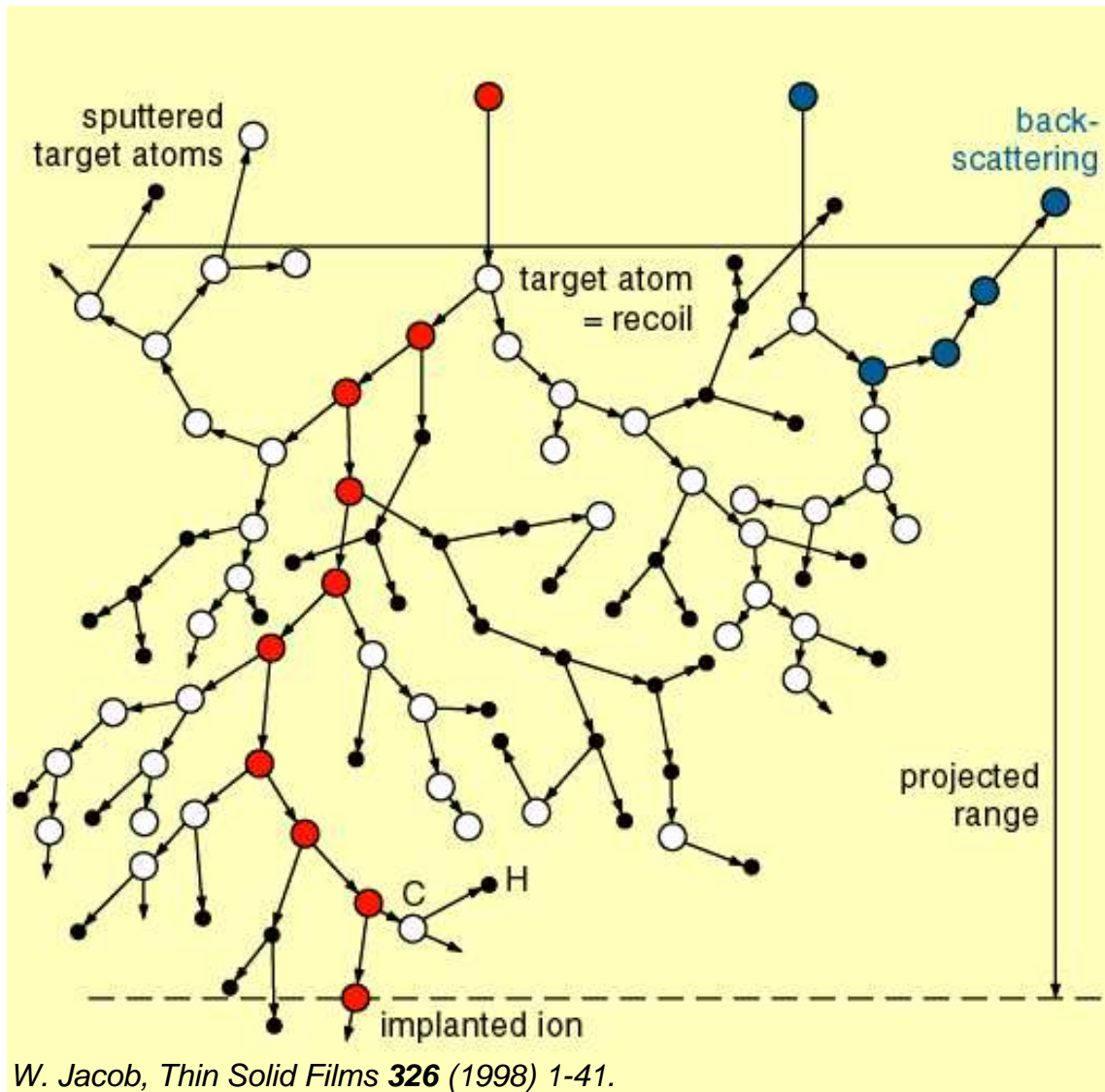
energy transfer:

$$T_{\max} = 4 M_1 M_2 / (M_1 + M_2)^2$$

→ isotope effect

Open questions / problems:

- molecular ions ↔ atomic ions (at low and high energy)
(most data are measured using H_2^+ or H_3^+ ions!)
- surface roughness (dynamical development during process)



W. Jacob, *Thin Solid Films* **326** (1998) 1-41.

Schematic representation of C impinging on a-C:H

Relevant processes:

- sputtering
- implantation
- backscattering
- displacement

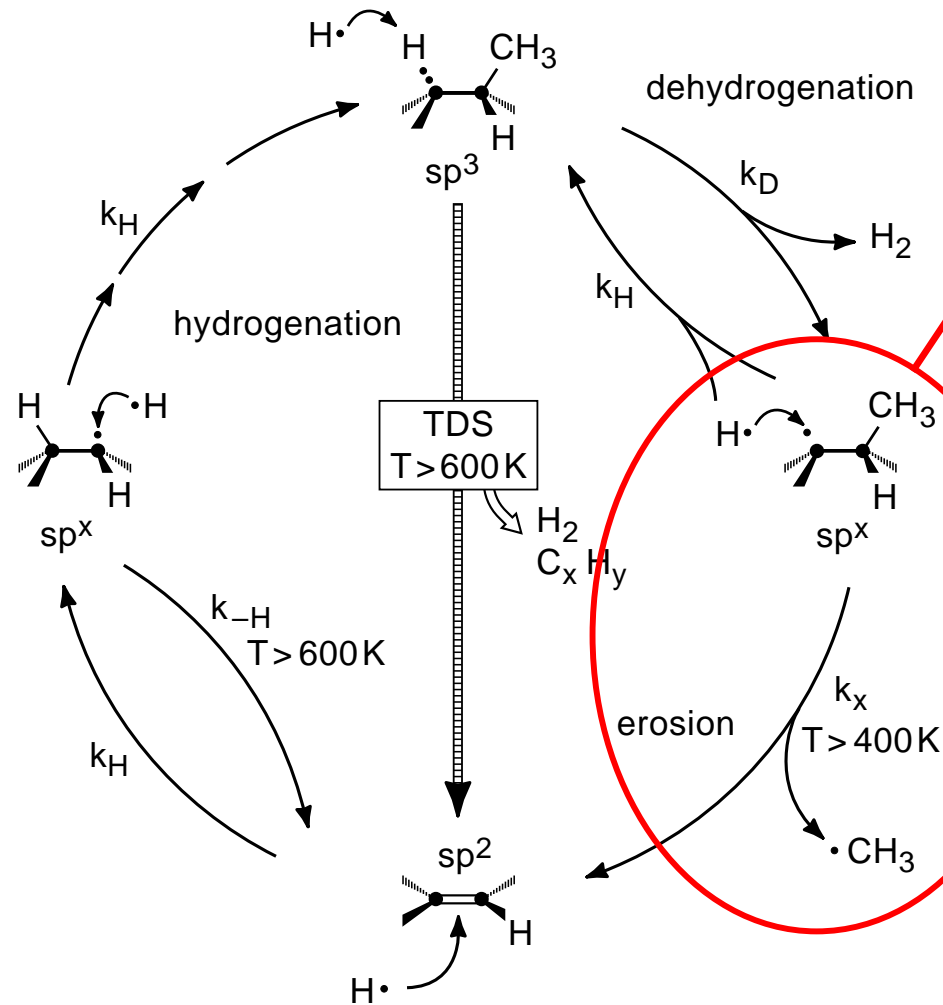
Elastic energy loss:

due to collisions with the nuclei
(= nuclear energy loss)

Inelastic energy loss:

due to energy transfer to the electrons,
continuous along the path,
no change of direction

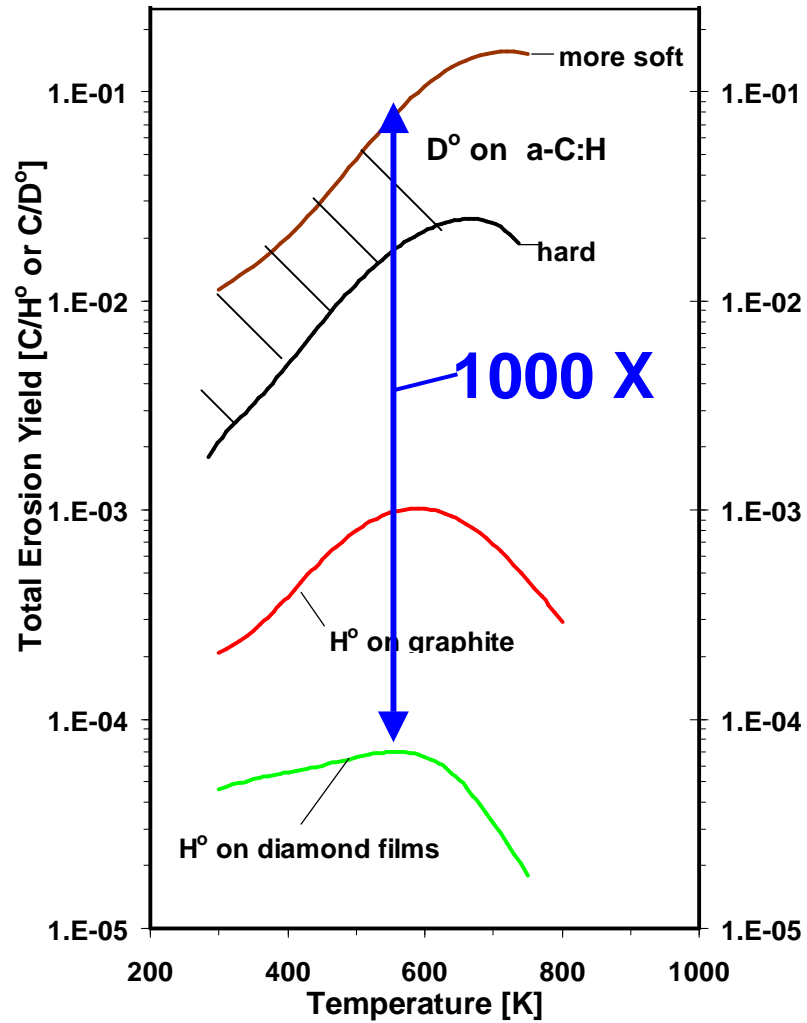
H-atom induced chemical erosion



Thermally-activated release of CH₃

Precursor for chemical erosion is a CH₃ group adjacent to a dangling bond site both are produced by interaction with atomic hydrogen

E.Vietzke et al., Surf. Coat. Technol. 47 (1991)156



Three orders of magnitude difference in total erosion.

→ reactivity of the surface depends critically on the surface structure.

Sputtering with reactive ions: physics meets chemistry

H and D bombardment of carbon

Chemical erosion, ion-induced chemical erosion, ion-enhanced chemical erosion, ion-induced etching, reactive ion etching, chemically enhanced physical sputtering, chemical sputtering, ...

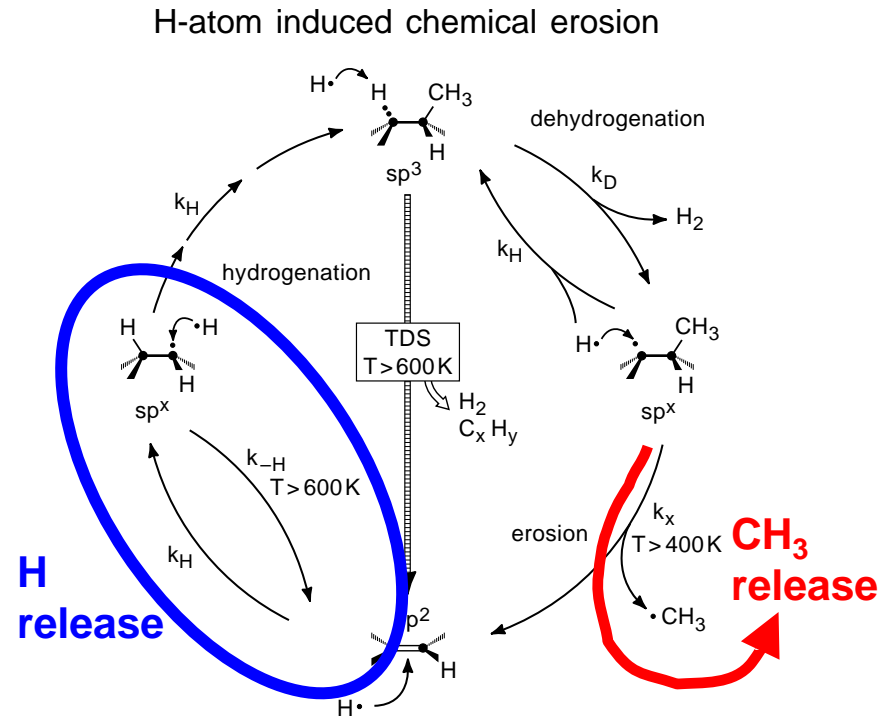
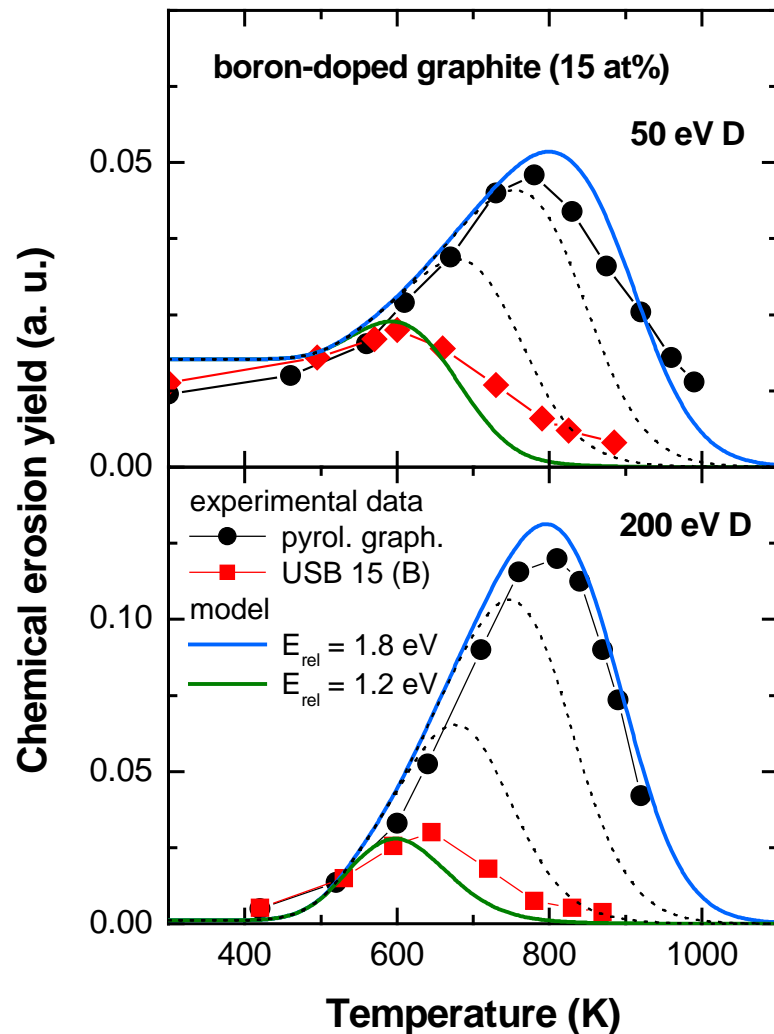
A simple picture:

Chemical reactions take place at the end of range, when H isotopes are thermalized.

Molecules are formed locally, then they diffuse to the surface and desorb.

→ temperature dependence of process

Chemical erosion: T dependence and influence of doping

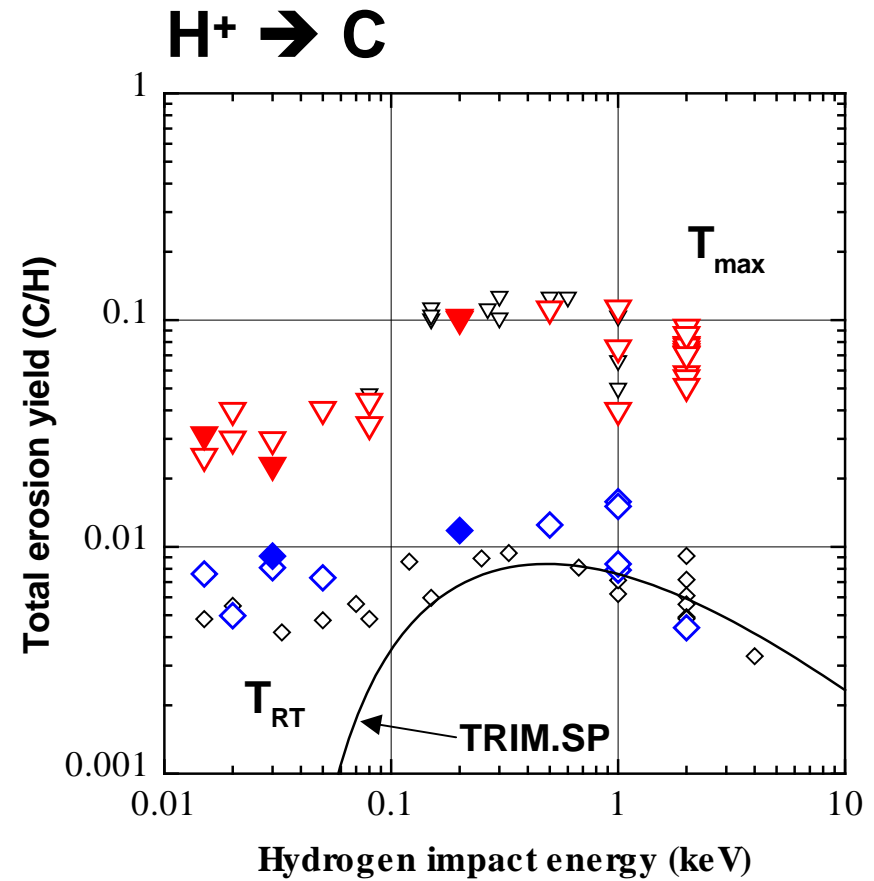
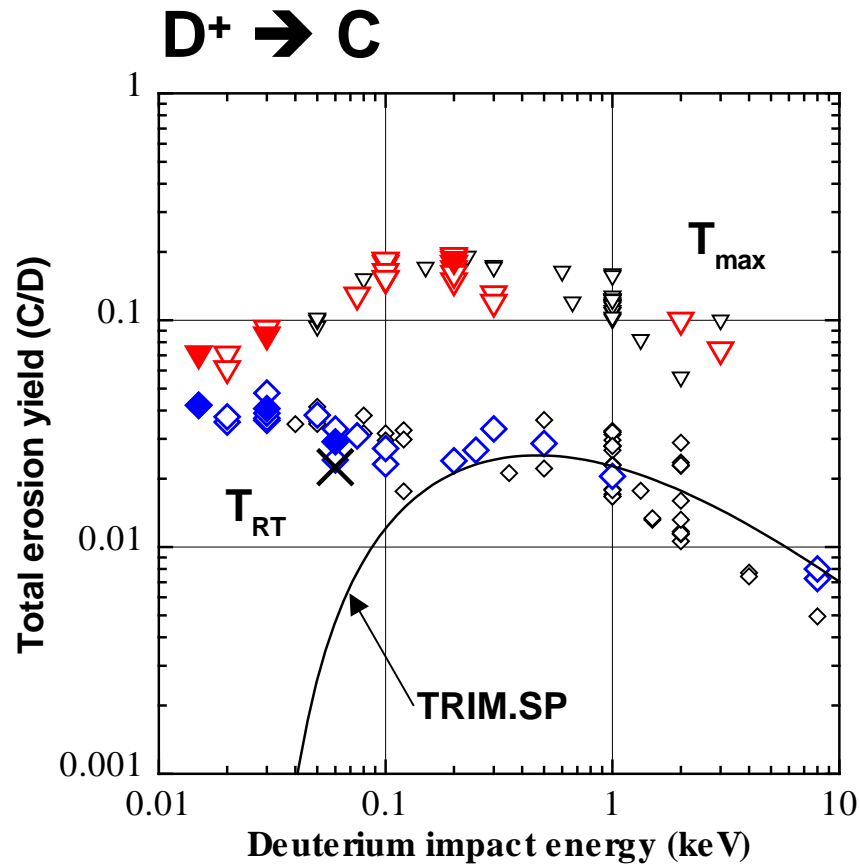


Maximum in erosion yield = competition between **H release** ($T_{act} = 1.8 \text{ eV}$) and **CH₃ release** ($T_{act} = 1.6 \text{ eV}$).

Doping reduces T_{act} for H release
 → interruption of chemical erosion cycle

C. García-Rosales, J. Roth, J. Nucl. Mater. **196-198** (1992) 573.

Chemical sputtering of carbon: D, H → C

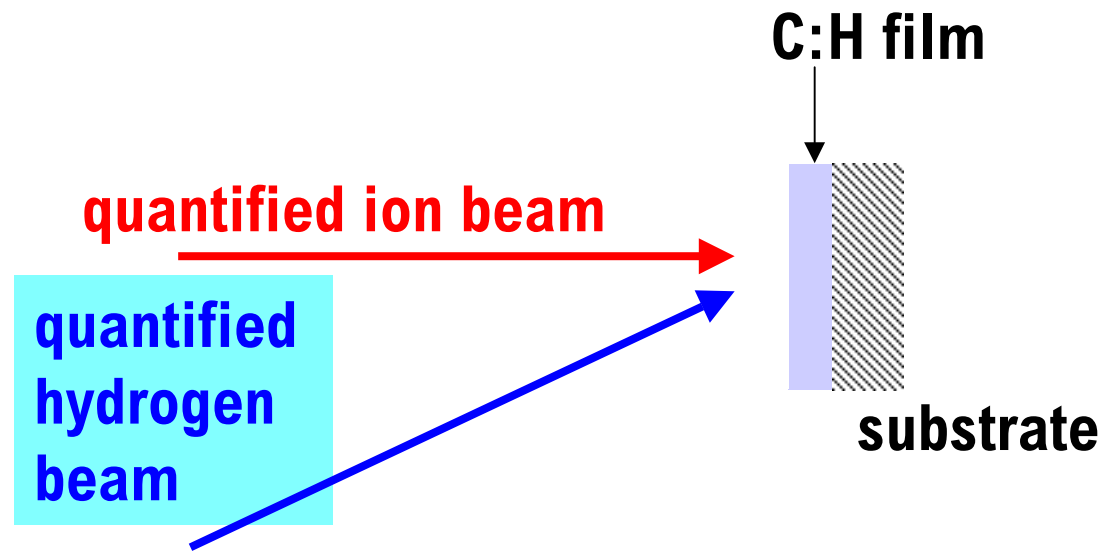


M. Balden, J. Roth, *J. Nucl. Mater.* **280**, 39-44 (2000)

New weight-loss measurements of the chemical erosion yields of carbon materials under hydrogen ion bombardment

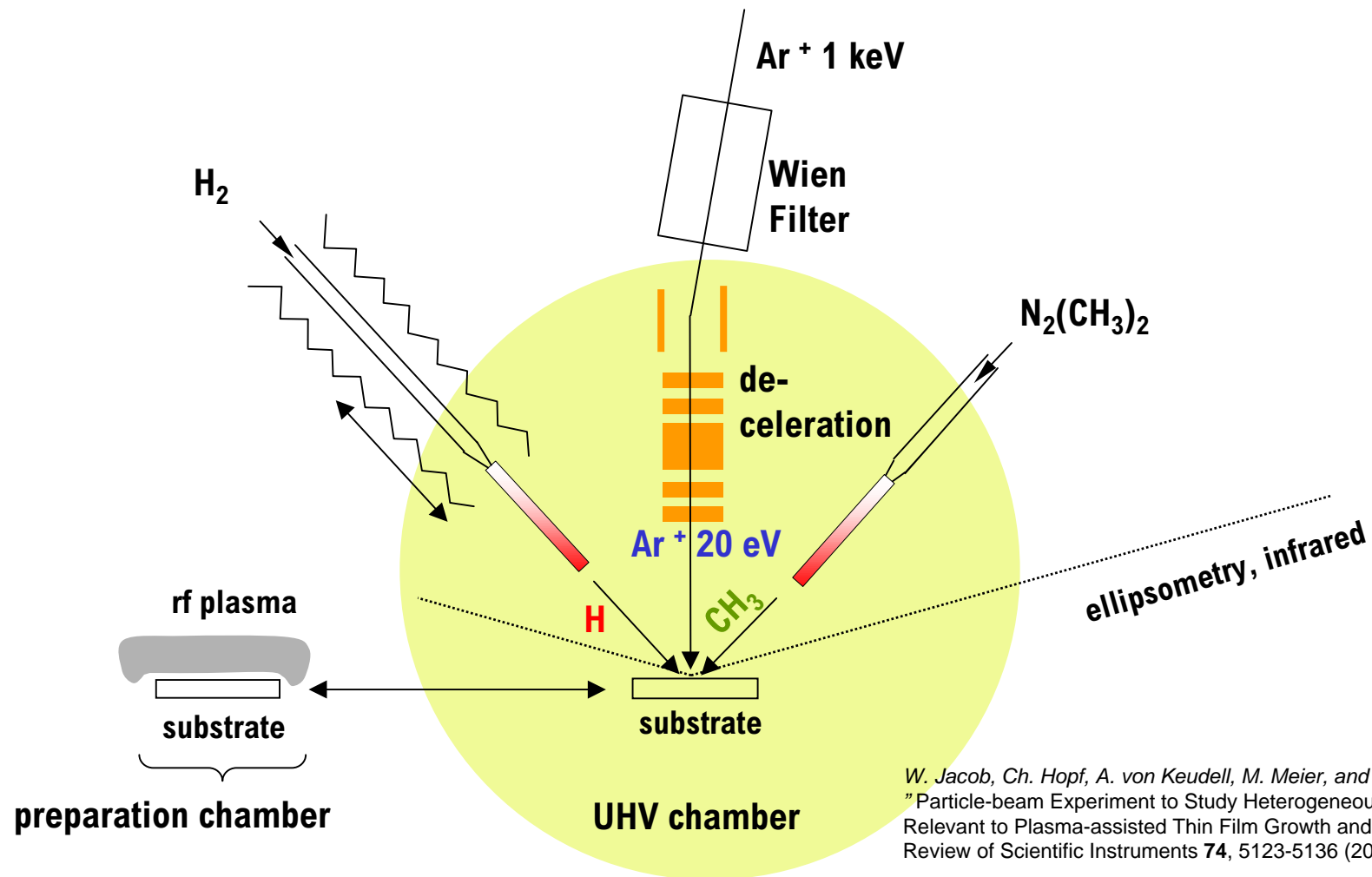
Particle-beam experiments

Chemical sputtering



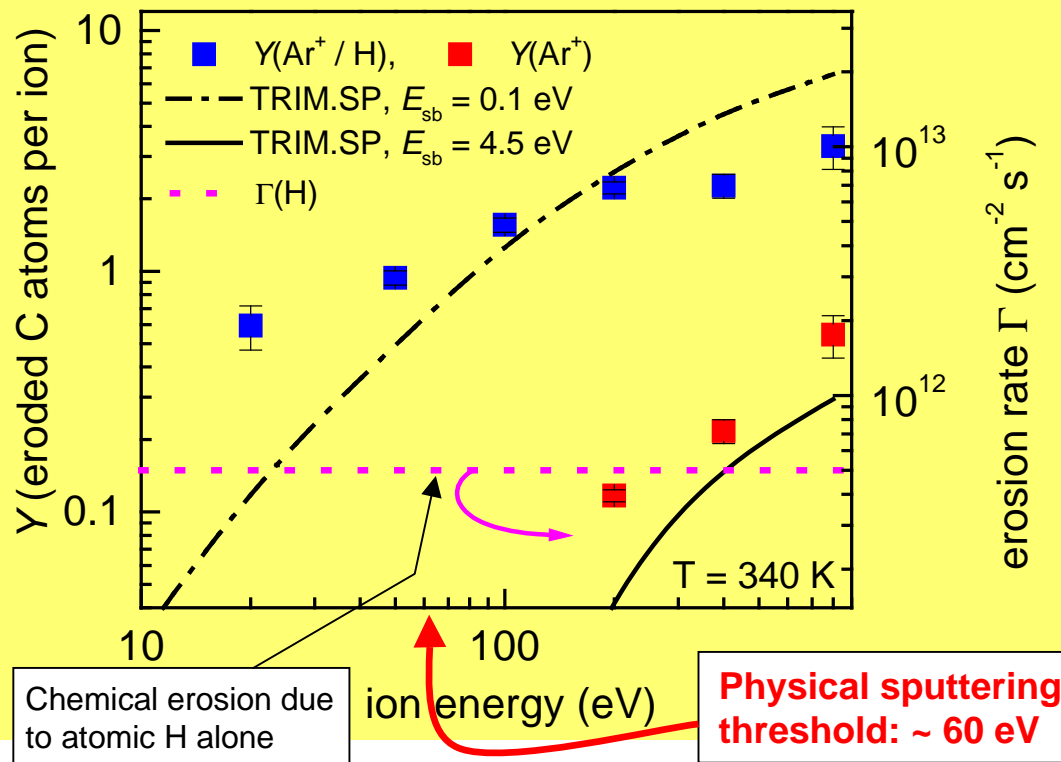
$$\text{erosion yield} = \frac{\text{measured erosion rate in eroded carbon atoms per cm}^{-2}\text{s}^{-1}}{\text{impinging ion flux per cm}^{-2}\text{s}^{-1}}$$

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).

Chemical Sputtering



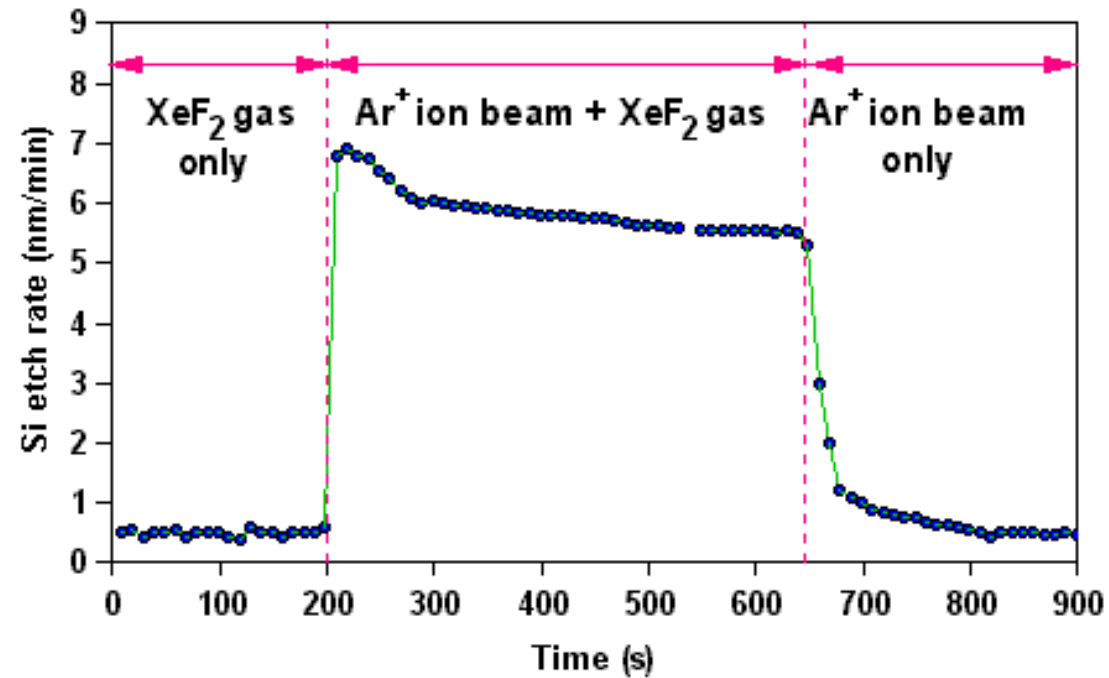
Erosion of a-C:H layers

comparison of simple **physical sputtering** (red symbols) due to Ar ions with erosion due to simultaneous interaction of H and Ar⁺ (blue symbols).

- enhanced erosion above 200 eV for simultaneous interaction
- erosion below threshold for physical sputtering (threshold energy for physical sputtering $\approx 60 \text{ eV}$)
- erosion at 20 eV \gg pure chemical erosion \Rightarrow '**chemical sputtering**'

- separation of chemical and kinematical effects due to use of Ar⁺ and H
- neutral / ion ratio ≈ 400

Christian Hopf, PhD Thesis
 Ch. Hopf, A. von Keudell, and W. Jacob,
 "Chemical Sputtering of Hydrocarbon Films by Low-energy Ar⁺ Ions and H Atom Impact",
 Nuclear Fusion **42**, L27 (2002).
 Ch. Hopf, A. von Keudell, and W. Jacob, "Chemical Sputtering of Hydrocarbon Films",
 J. Appl. Phys. **94**, 2373 (2003).

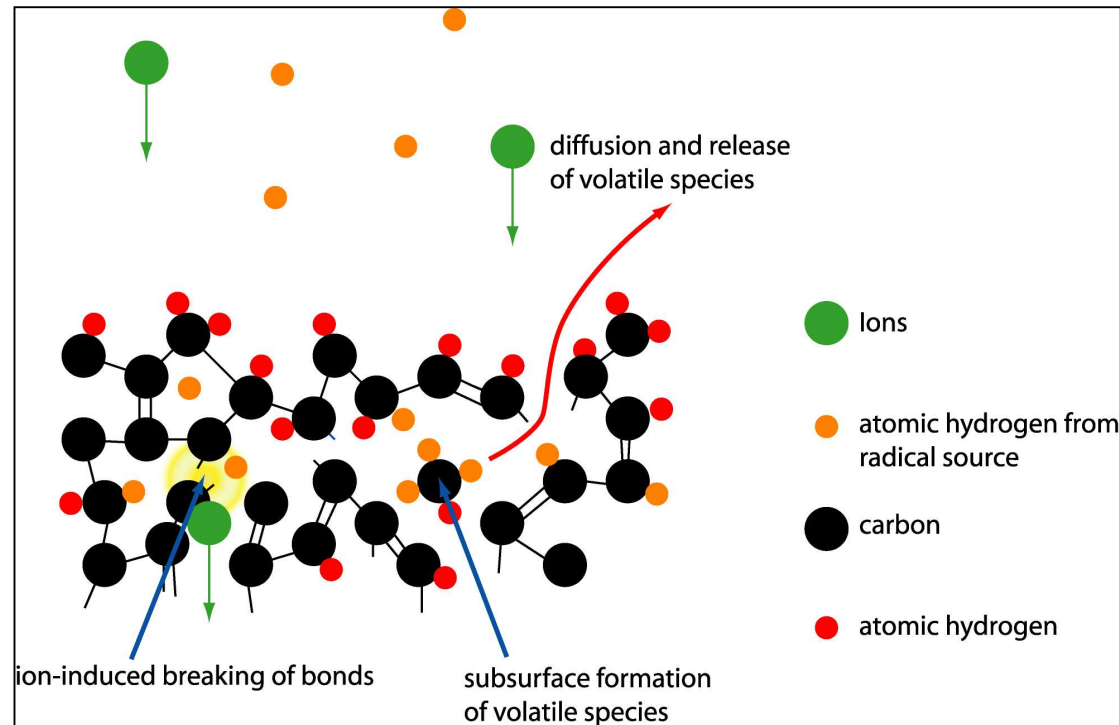


J.W. Coburn, H.F. Winters, J. Appl. Phys. 50 (1979), 3189

H.F. Winters, J.W. Coburn, Surface Science Reports 14 (1992) 162

H.F. Winters, J.W. Coburn, Surface Science Reports **14** (1992) 162:

For the propose of this paper "Chemical sputtering" is defined as 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 desorbed in the gas phase. The key process leading to desorption is the chemical reaction. The collision cascade physics ... is operative in inducing the chemical reaction.



- ions break C—C bonds
- H passivates broken bonds
- (1) and (2) → formation of volatile hydrocarbons below the surface
- diffusion of CH compounds to the surface and desorption

Energy dependence

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

bond breaking due to ion impact

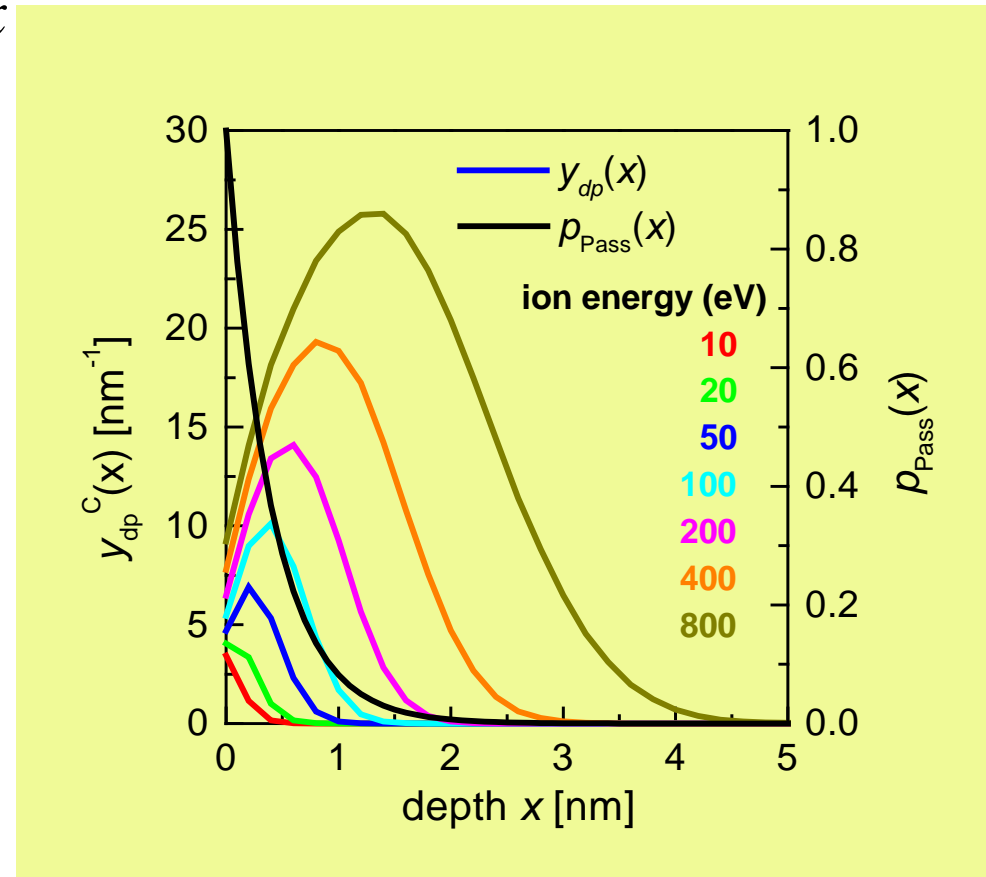
passivation by atomic H

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

displacement events per depth interval calculated by TRIM.SP

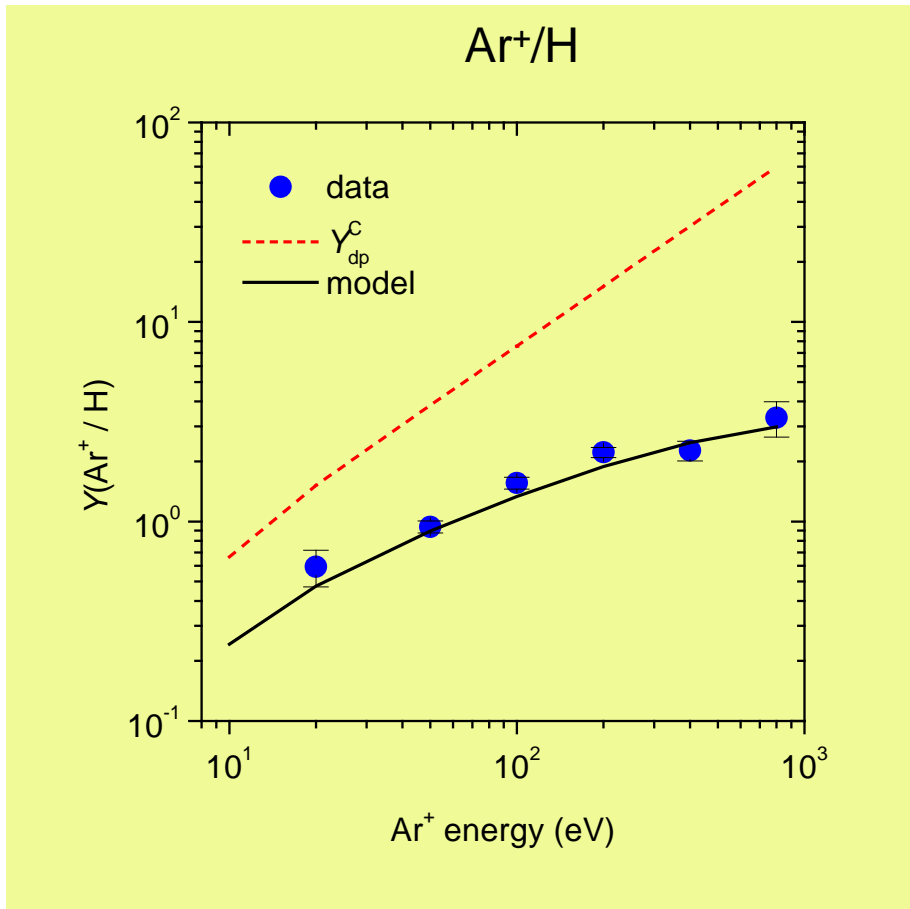
exponential decay, maximum range about 2 nm, known from plasma experiments

a is a fit parameter

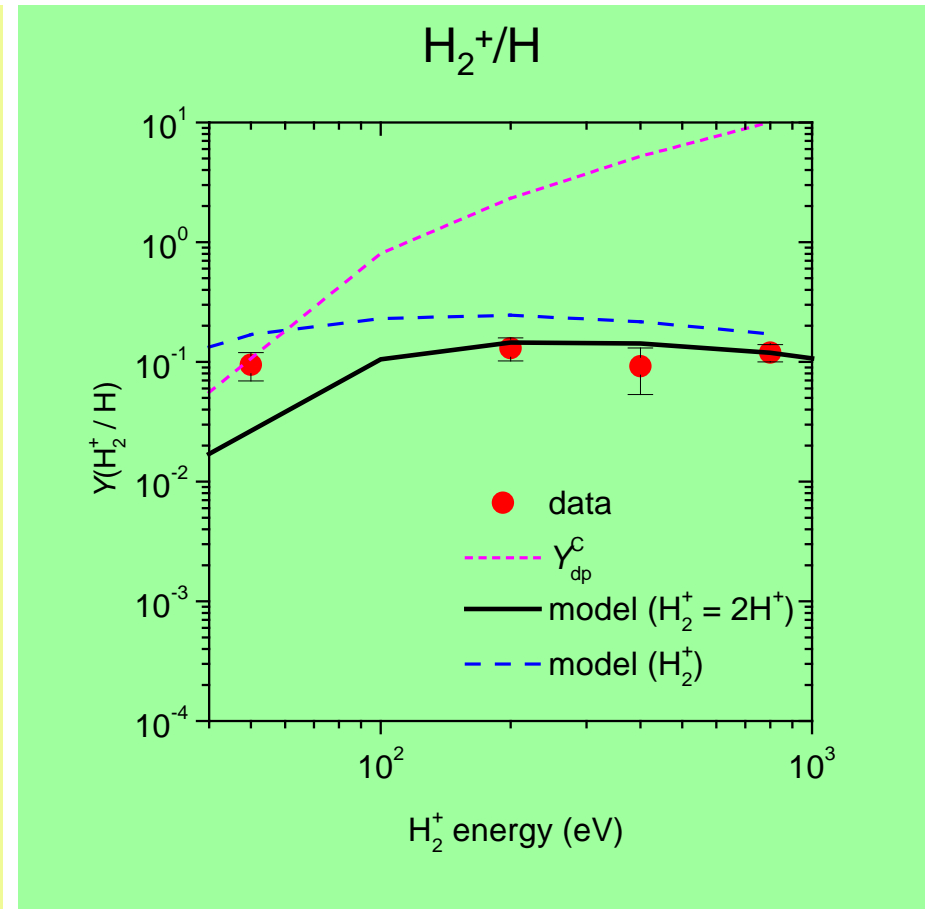


$$E_{dp}^c = 5 \text{ eV}, \lambda = 0.4 \text{ nm}$$

Energy dependence



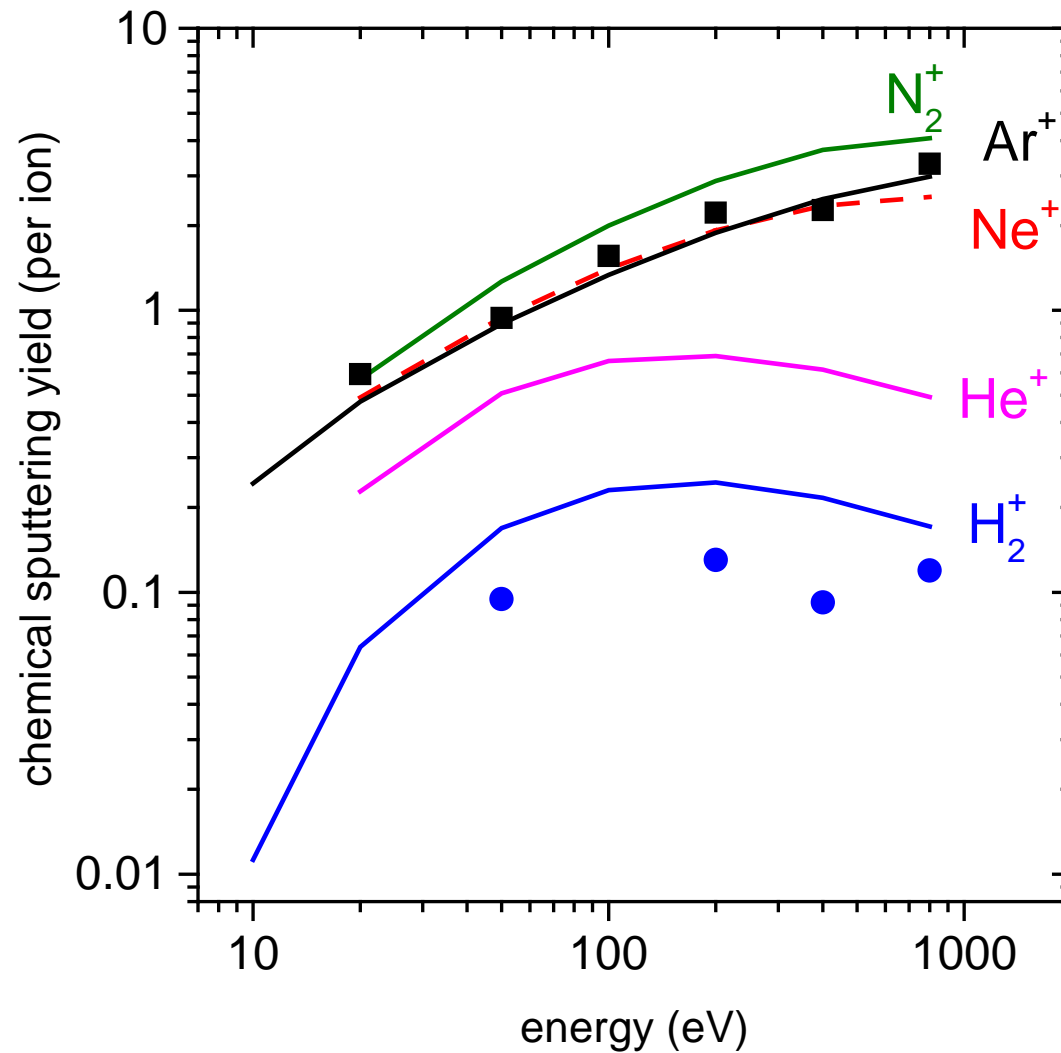
$a = 0.4$



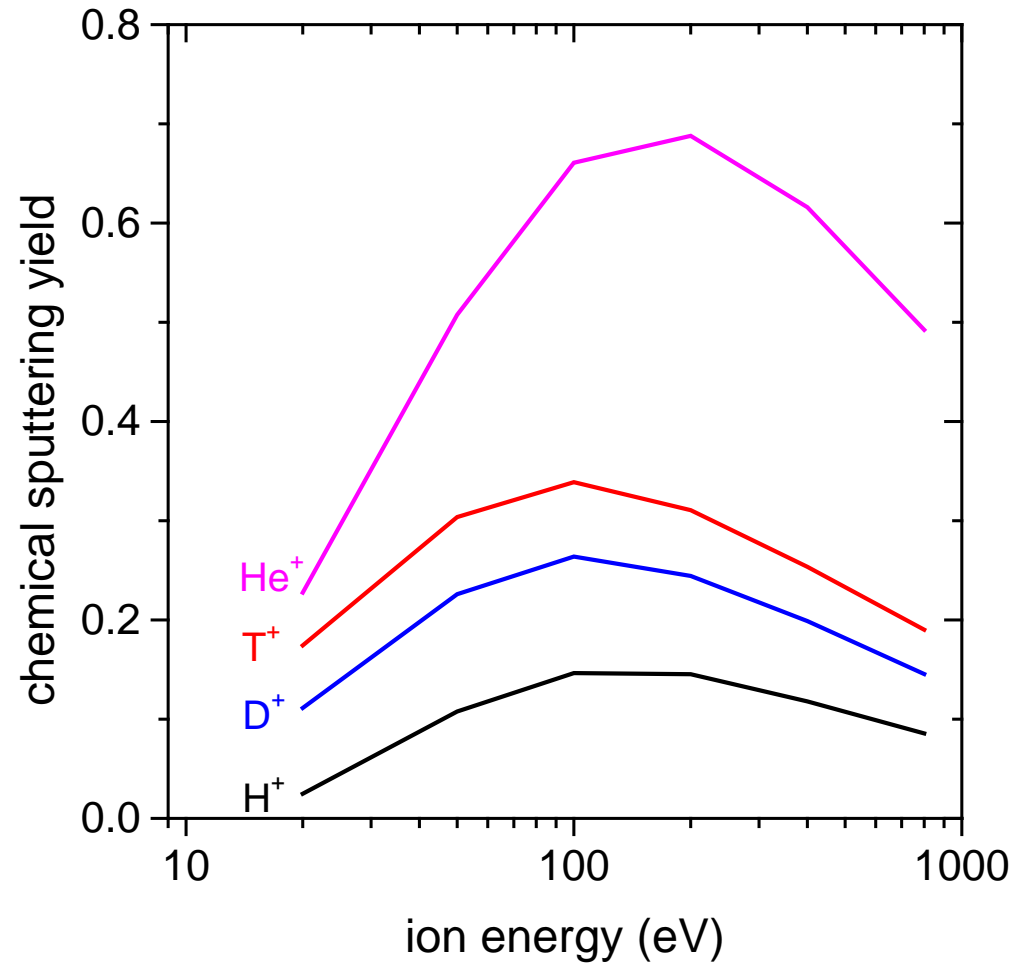
$a = 0.4$

$$j_H = 1.4 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}, j_{Ar^+} = 3.6 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}, R = j_H / j_{Ar^+} \approx 400$$

Energy dependence: Modeling results

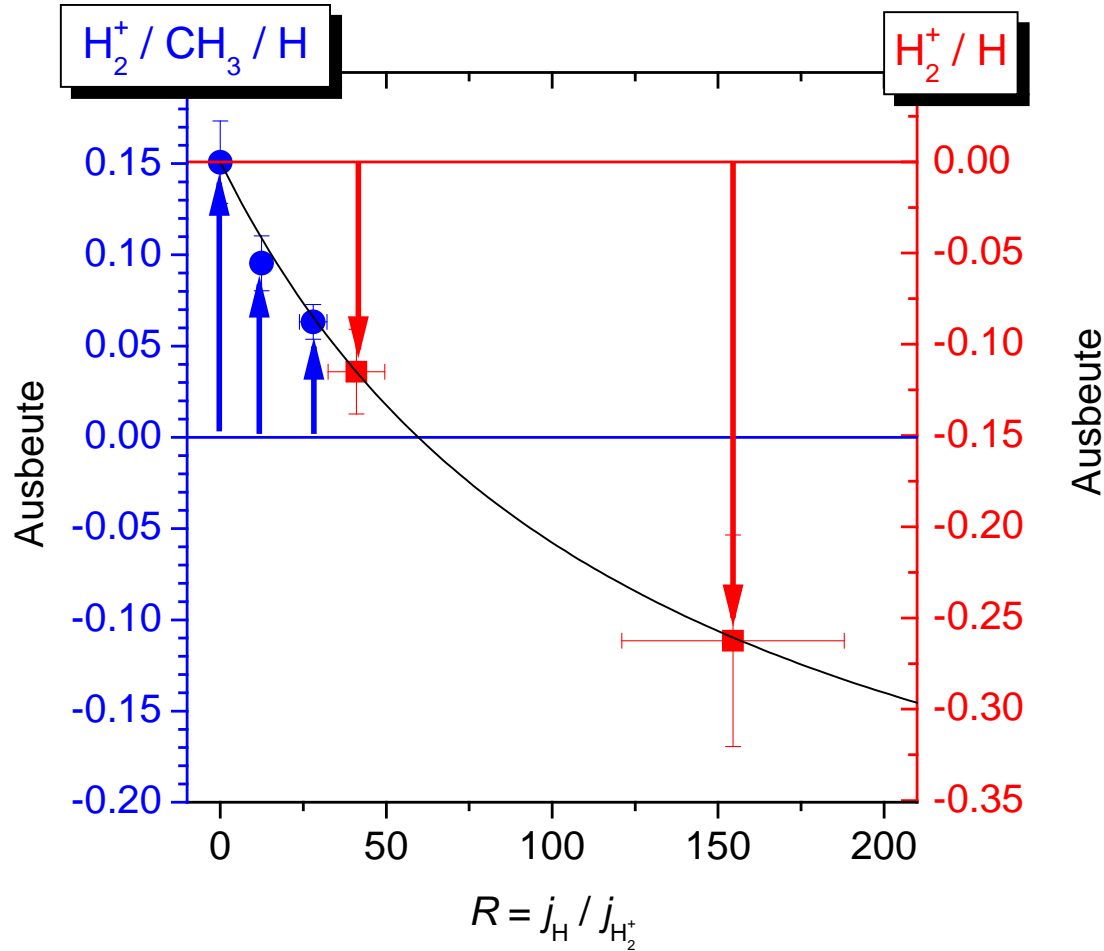


$a = 0.4$
 $R \approx 400$



$a = 0.4$
 $R \approx 400$

Growth competition: Deposition – chem. sputtering



Growth
 =
ion-induced sticking
 -
chemical sputtering

here:
 constant contribution from sticking
 -
 flux ratio dep. contribution from chemical sputtering

- **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 \times passivation
- predictions for other ions, e.g. H, D, T, He, N₂, ..

Growth of a-C:H is always a competition between deposition and erosion (chemical sputtering).

The end

Collaborators:

Christian Hopf

Achim von Keudell

Matthias Meier

Thomas Schwarz-Selinger