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

Plasma-surface interaction

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

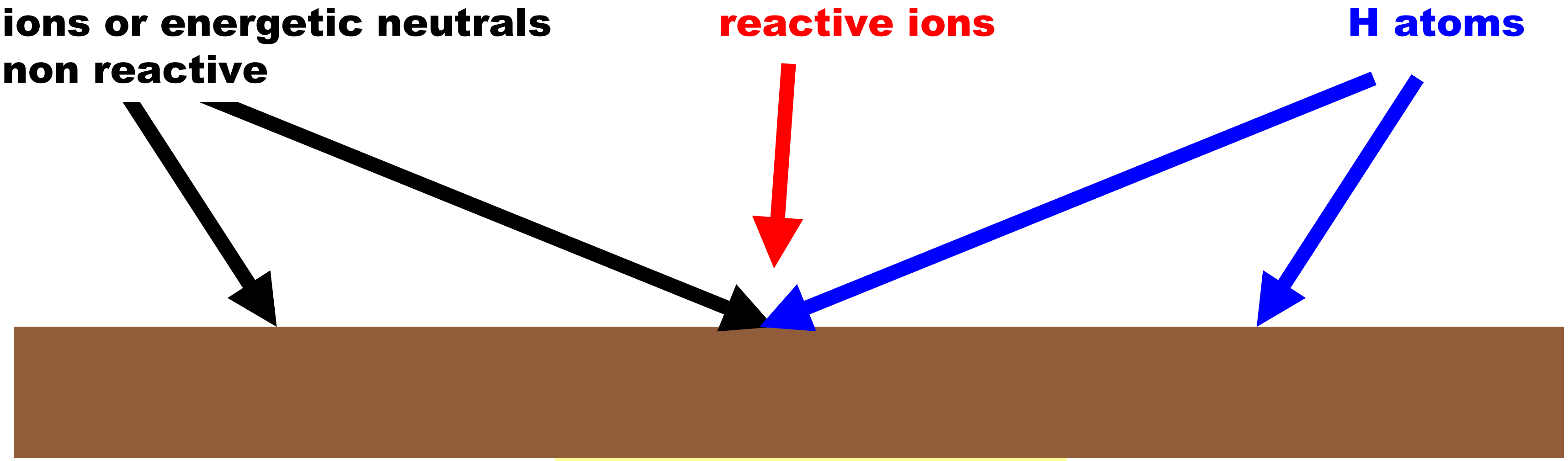
All these species show mutual interactions!

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

Ion/radical interaction

- ion/CH3 — "ion-induced stitching" postulated in literature **ion-induced sticking**
- ion/H — ion-induced etching (reactive ion etching, RIE) **chemical sputtering**

Chemical vs. physical sputtering



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 vs. physical sputtering

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:

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

$E_{mean} \approx$ some eV

Physical sputtering

- 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

energy transfer:

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

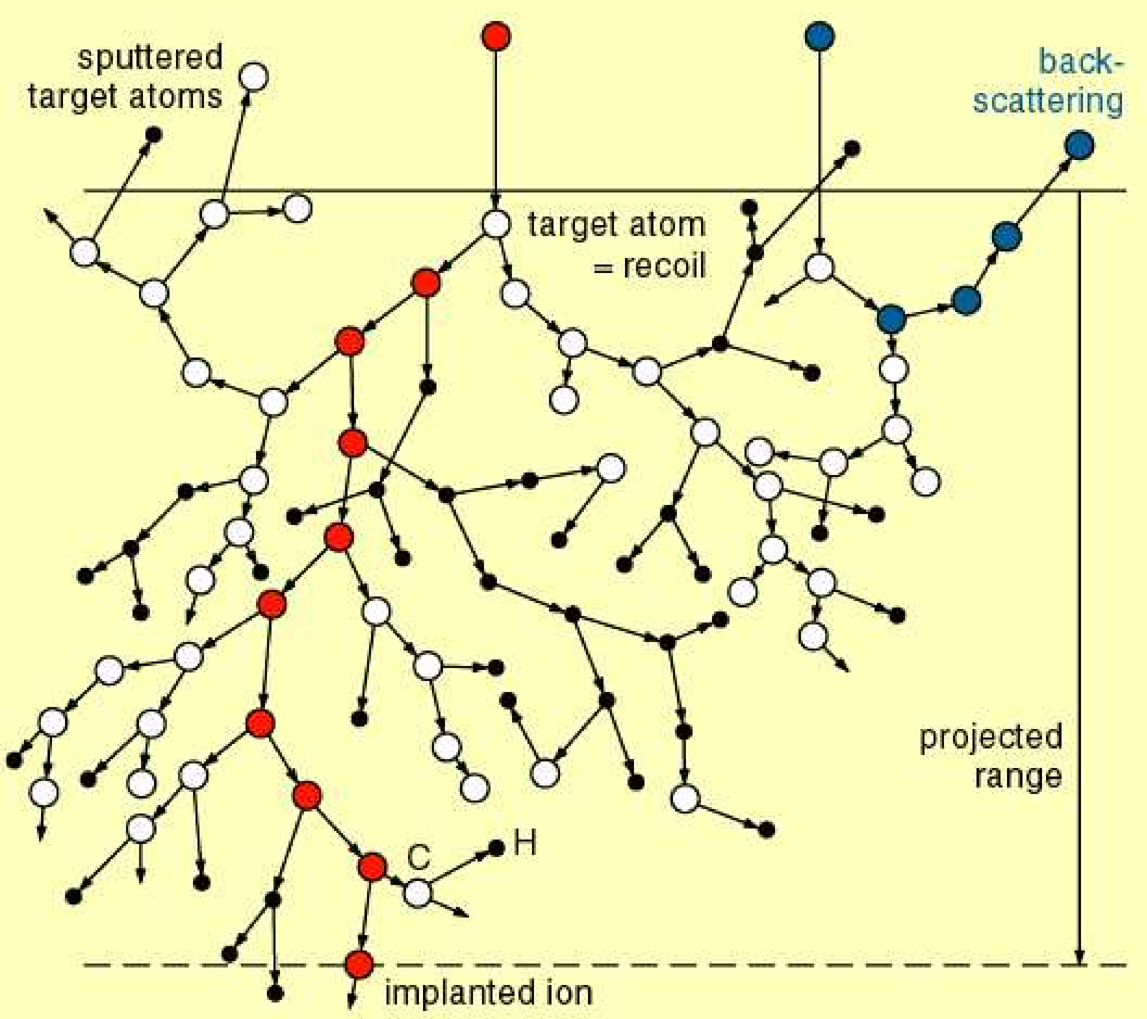
→ isotope effect

- threshold energy depends on target/projectile combination
- depends on angle of incidence
- depends on substrate material
- depends on target roughness

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)

Ion-solid interaction



*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:

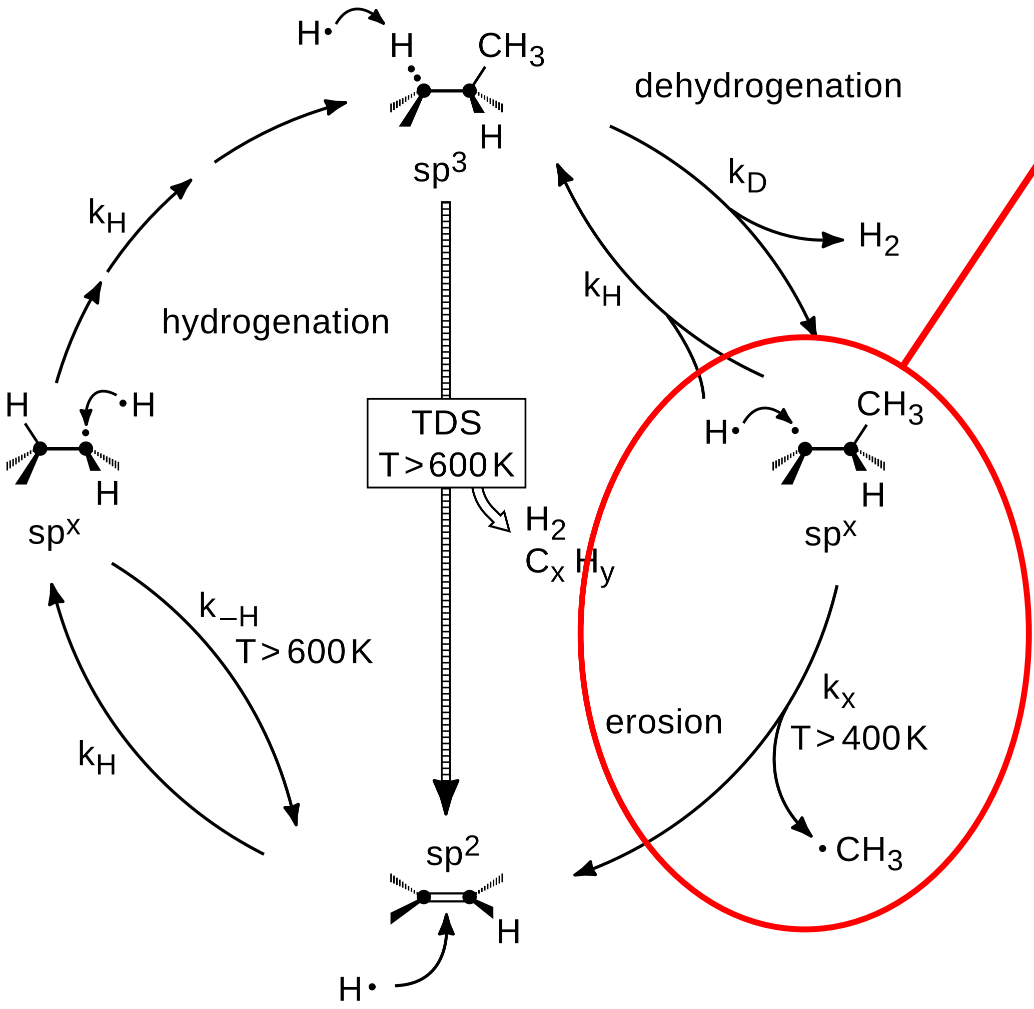
due to collisions with the nuclei (= nuclear energy loss)

Inelastic energy loss:

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

Chemical erosion

H-atom induced chemical erosion

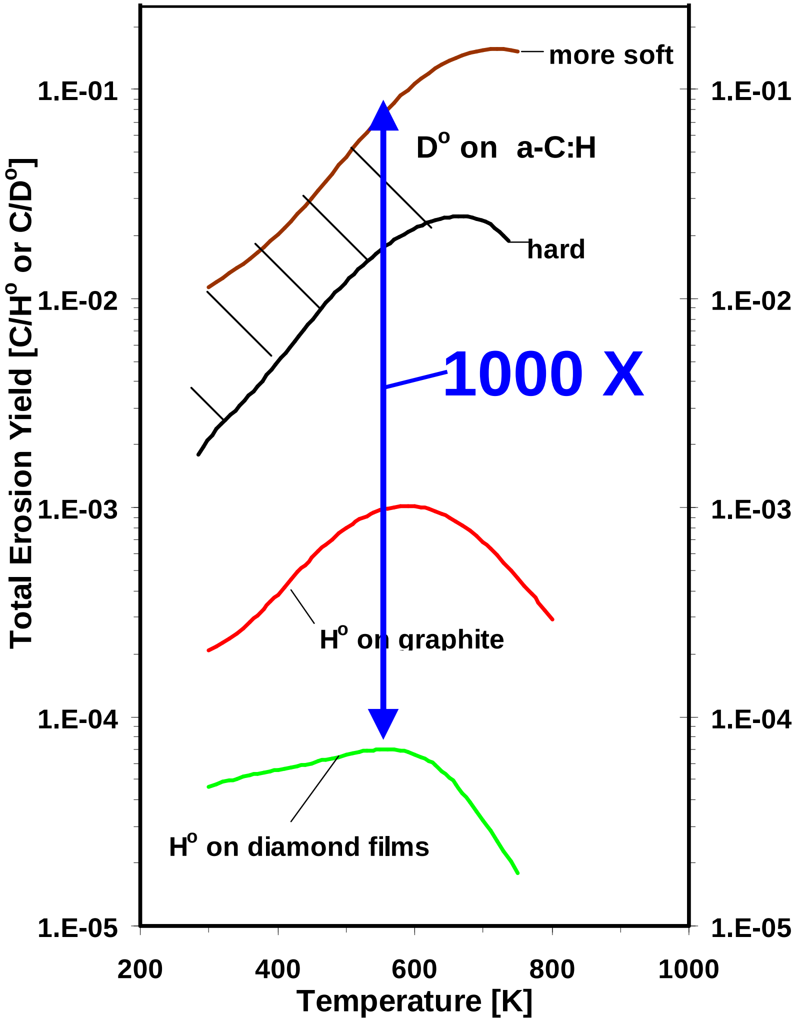


Thermally-activated release of CH_3

Precursor for chemical erosion is a CH_3 group adjacent to a dangling bond site
both are produced by interaction with atomic hydrogen

Chemical erosion

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

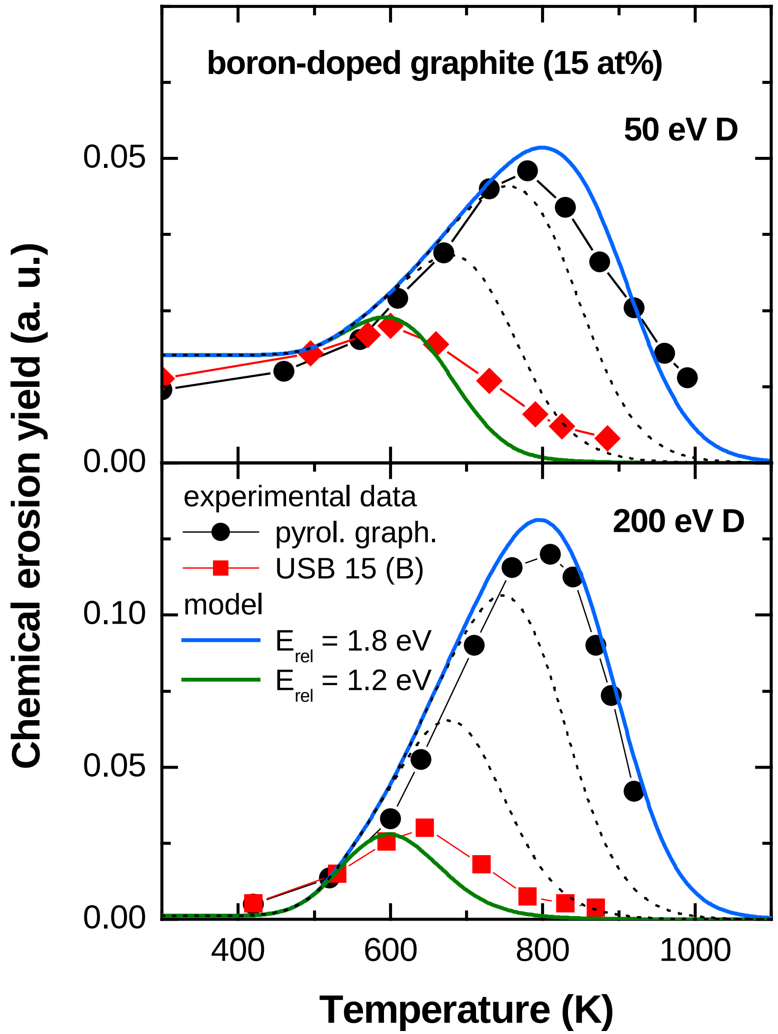
Chemical erosion, ion-induced chemical erosion, ion-enhanced chemical erosion, ion-induced etching, reactive ion etching, chemically enhanced physical sputtering, chemical sputtering, ...

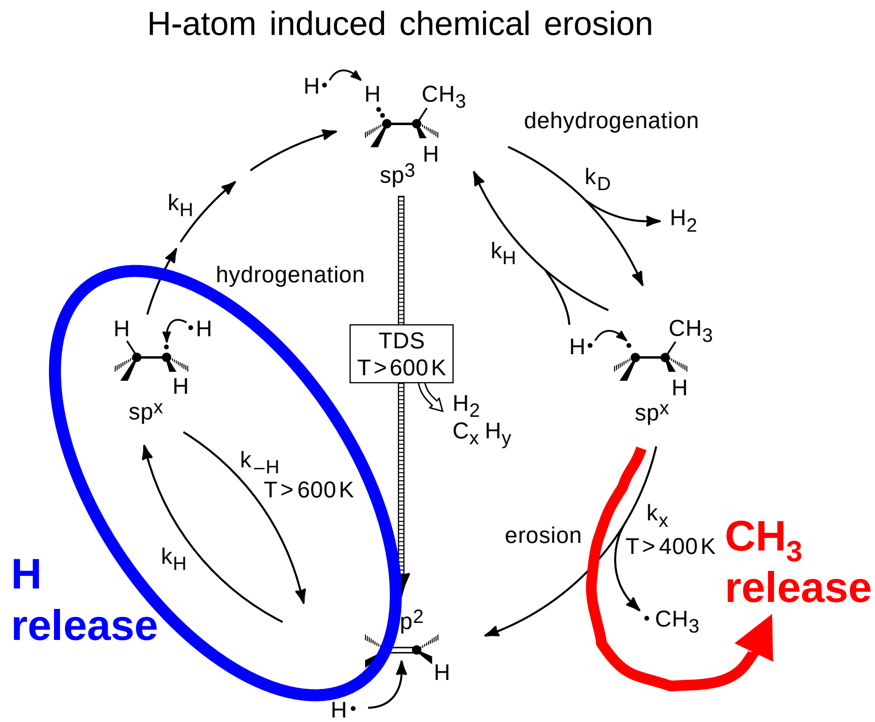
A simple picture:

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 eV) and CH_3 release (T_{act} = 1.6 eV).

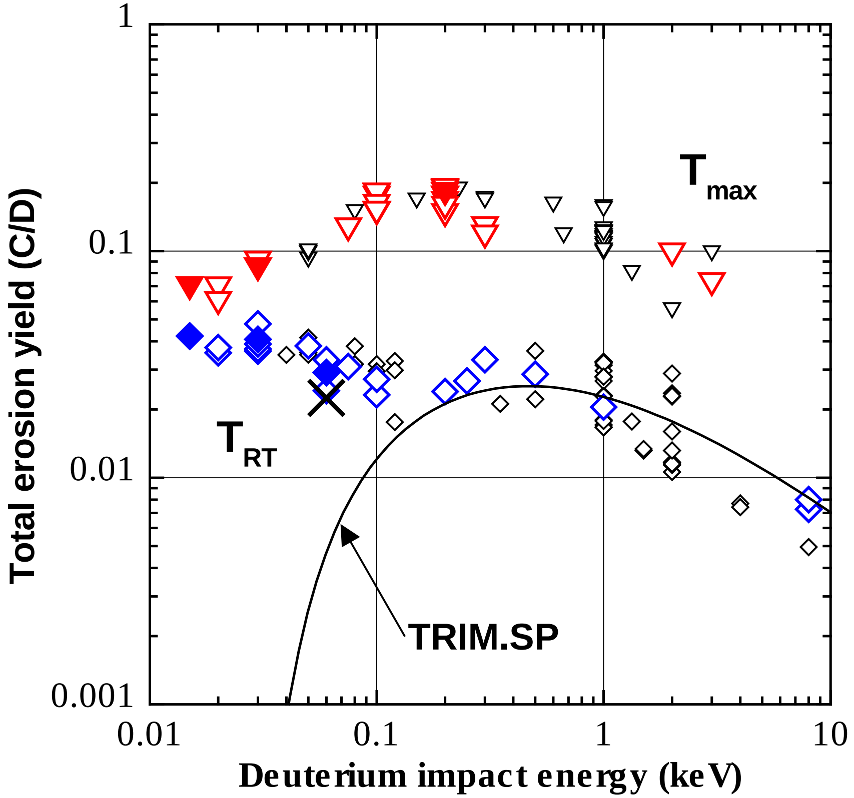
Doping reduces T_{act} for H release
→ interruption of chemical erosion cycle

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

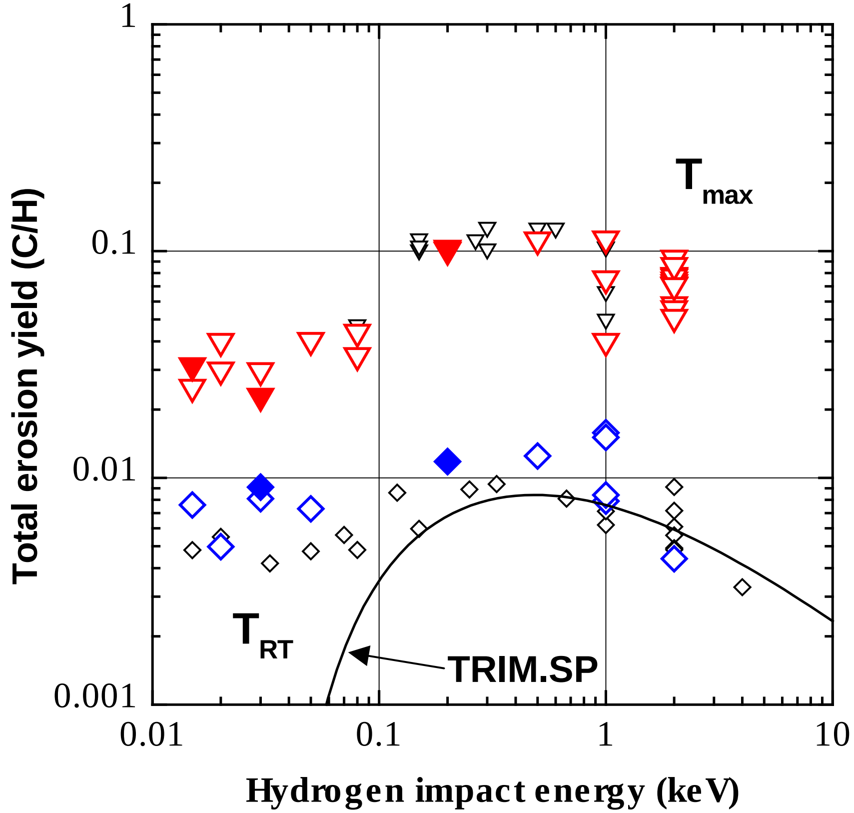
Chemical sputtering of carbon: D, H → C

CIPS

D^+ → C



H^+ → C



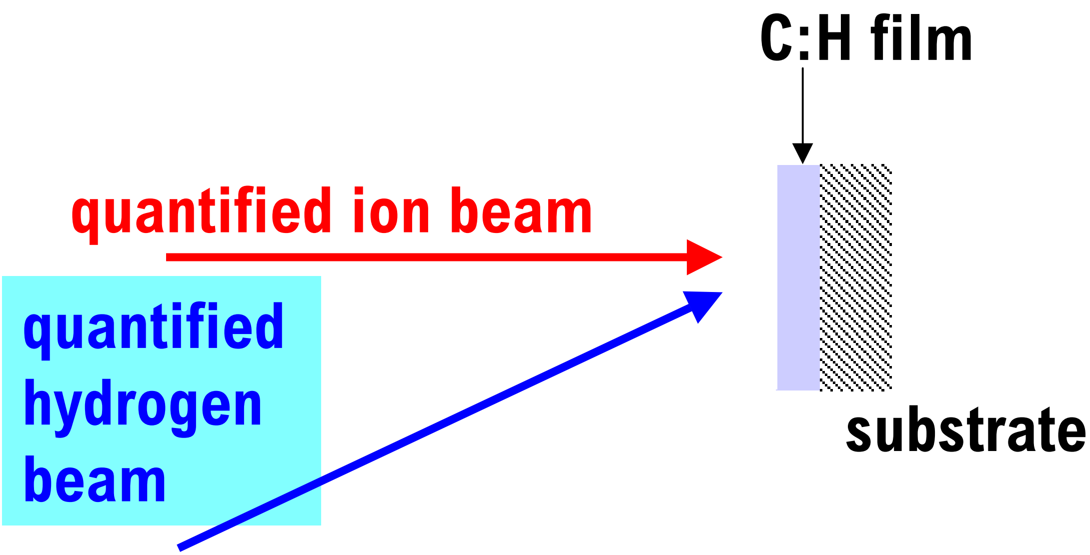
M. Balden, J. Roth, J. Nucl. Mater. ***280****, 39-44 (2000)*

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

Particle-beam experiments

Chemical sputtering

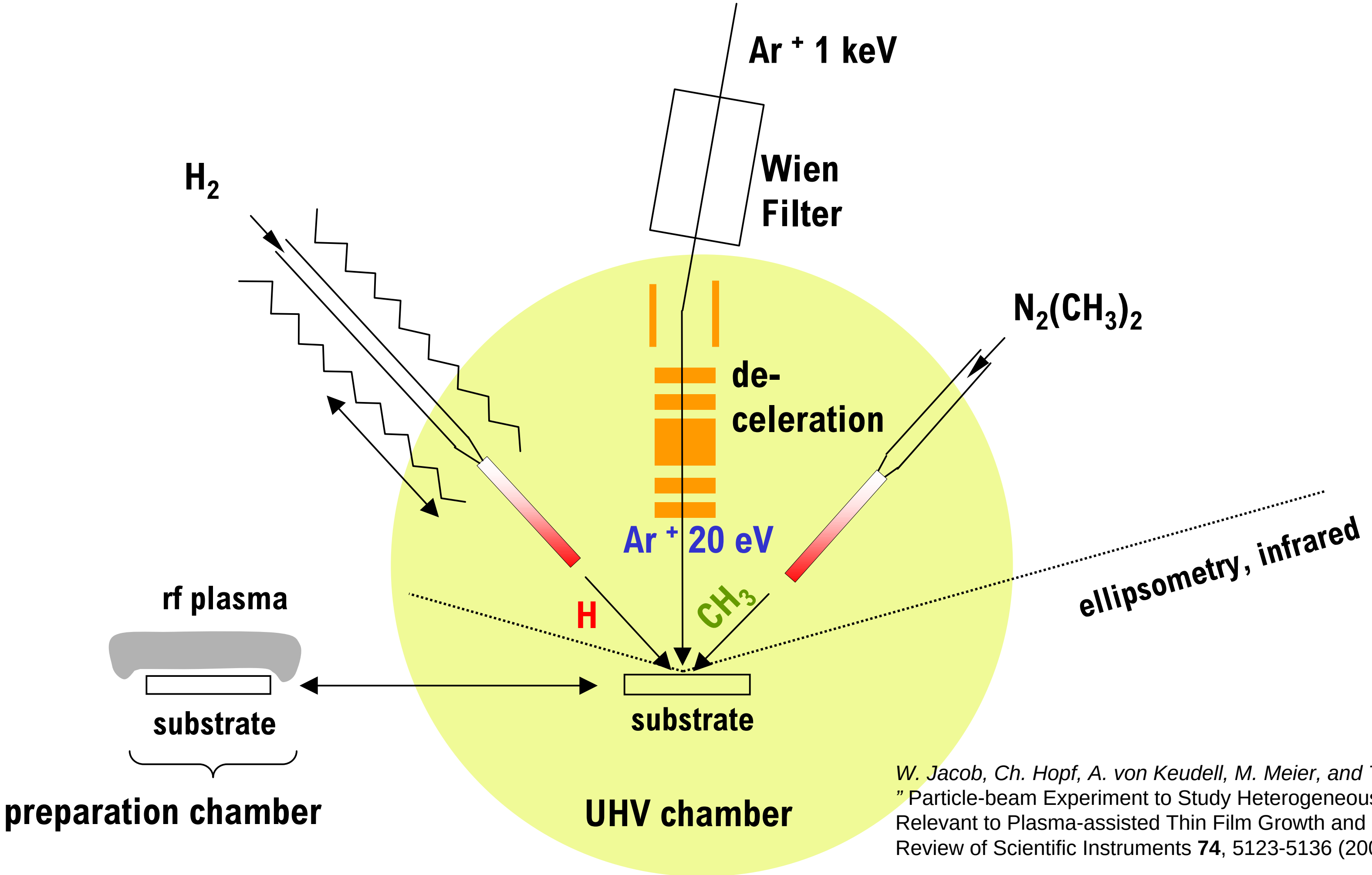
Measuring erosion yields



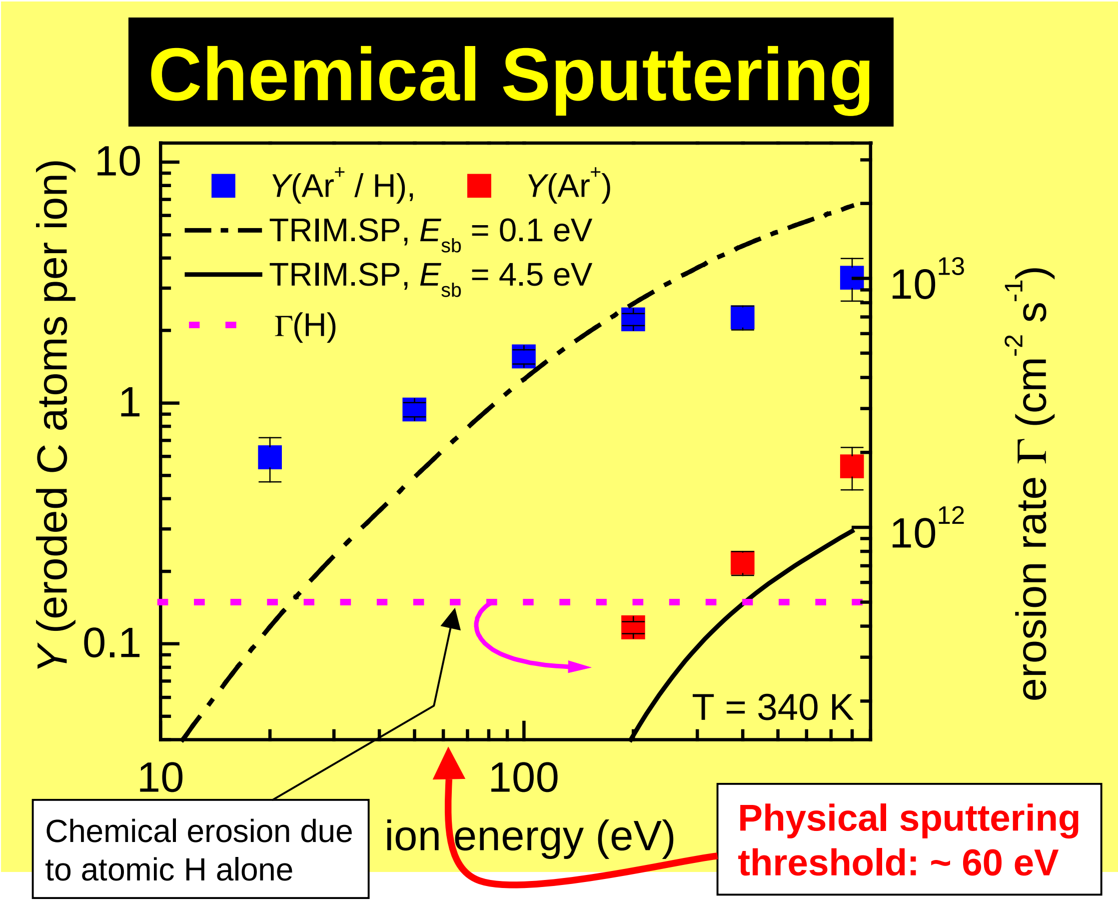
$$\text{erosion yield} = \frac{\text{measured erosion rate in eroded carbon atoms per } cm^{-2}s^{-1}}{\text{impinging ion flux per } cm^{-2}s^{-1}}$$

Experimental set-up

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).



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).*

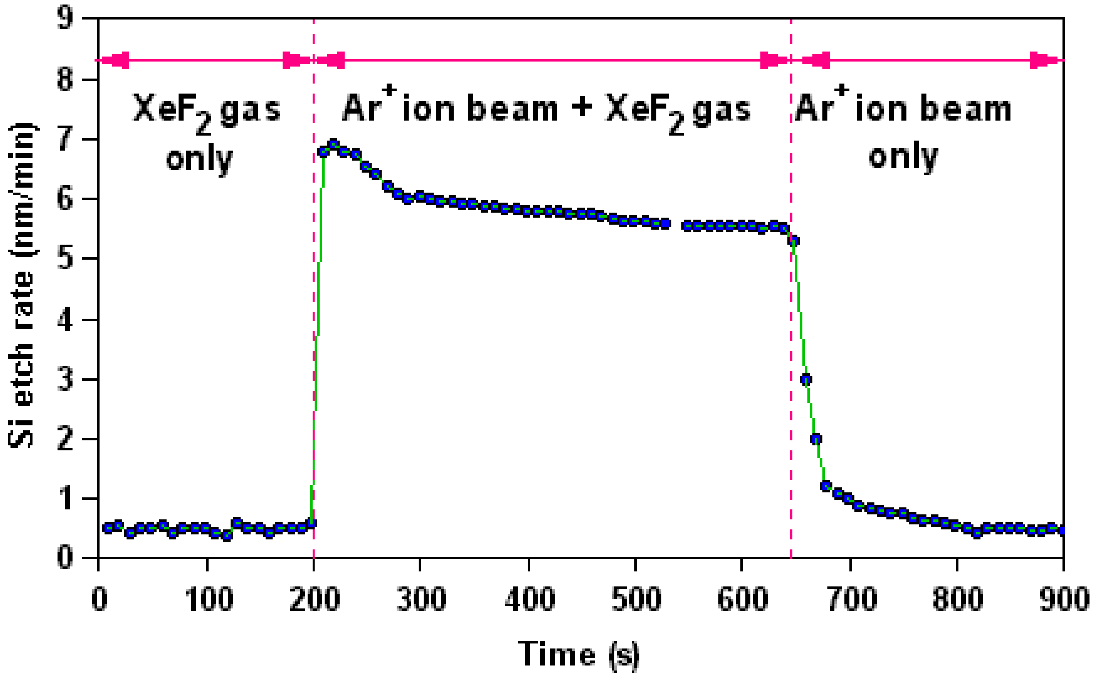
Erosion of a-C:H layers

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 ≈ 60 eV
- erosion at 20 eV >> pure chemical erosion ⇒ '***chemical sputtering***'

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

Chemical sputtering of silicon



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

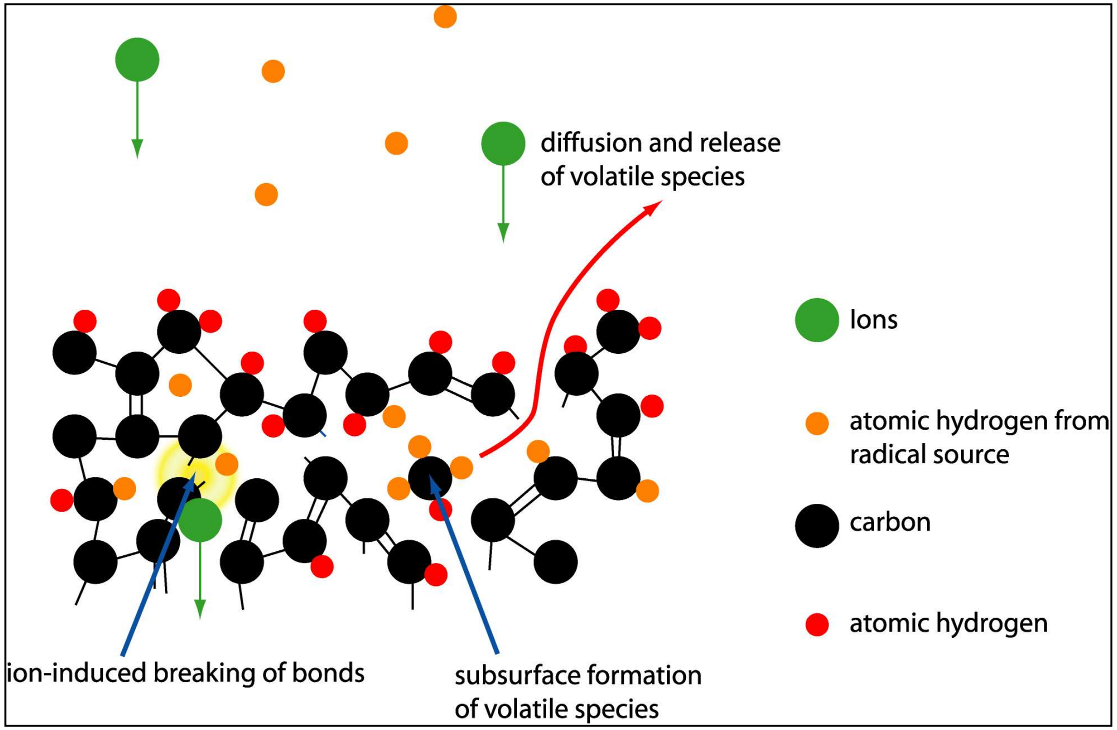
H.F. Winters, J.W. Coburn, Surface Science Reports 14 (1992) 162

Chemical sputtering: Definition

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.

Chemical sputtering mechanism



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

Energy dependence

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

bond breaking due to ion impact

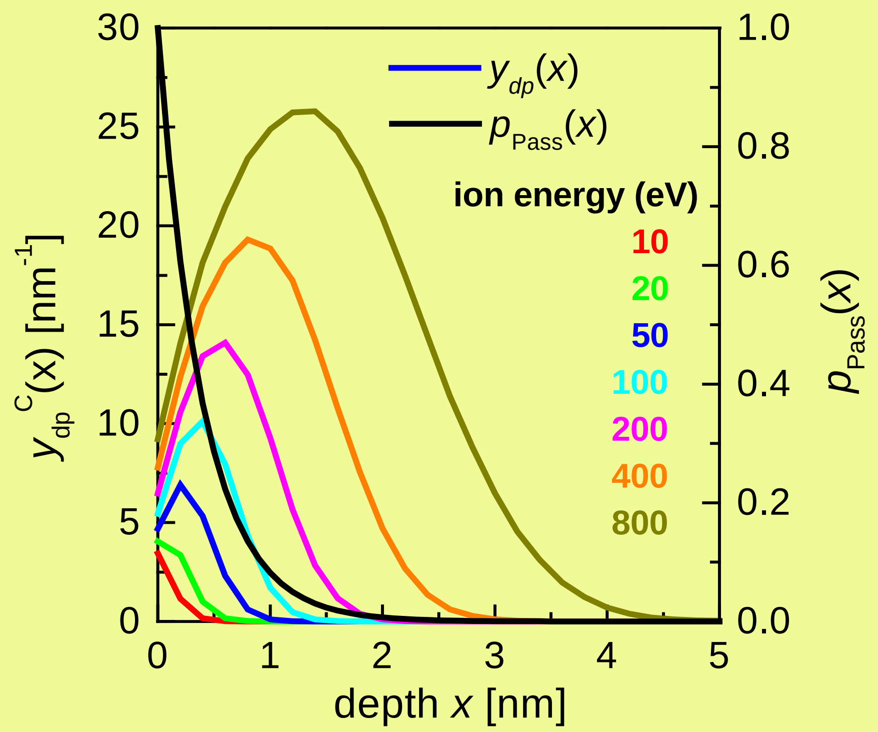
passivation by atomic H

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

displacement events per depth interval calculated by TRIM.SP

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

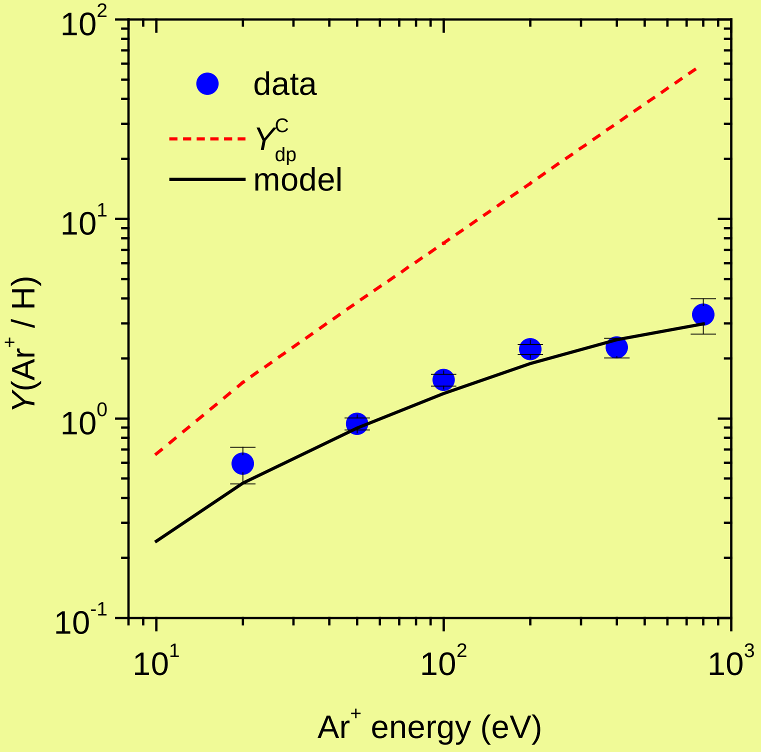
a is a fit parameter



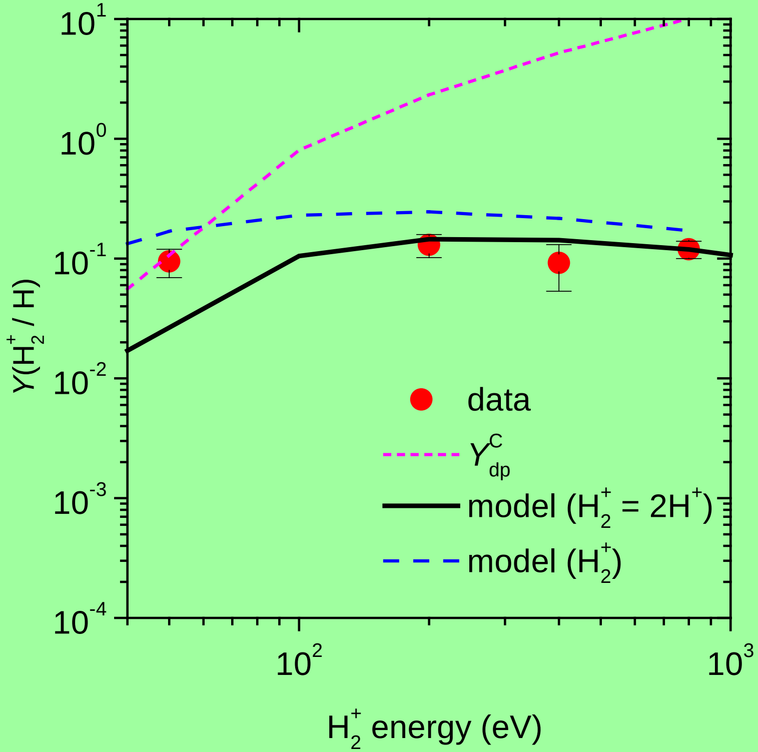
E_{dp}^{C} = 5 eV, λ = 0.4 nm

Energy dependence

Ar^+/H



H_2^+/H



a = 0.4

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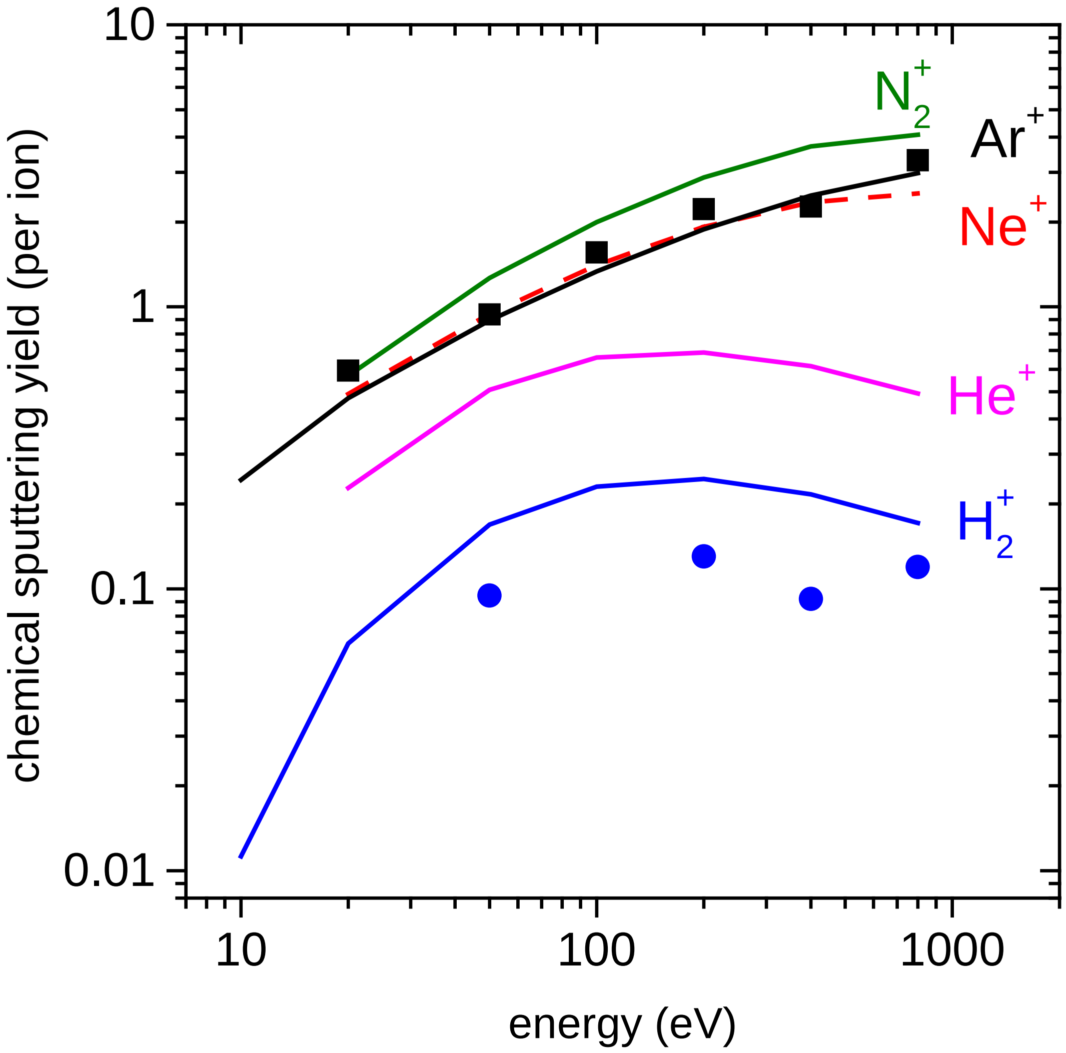
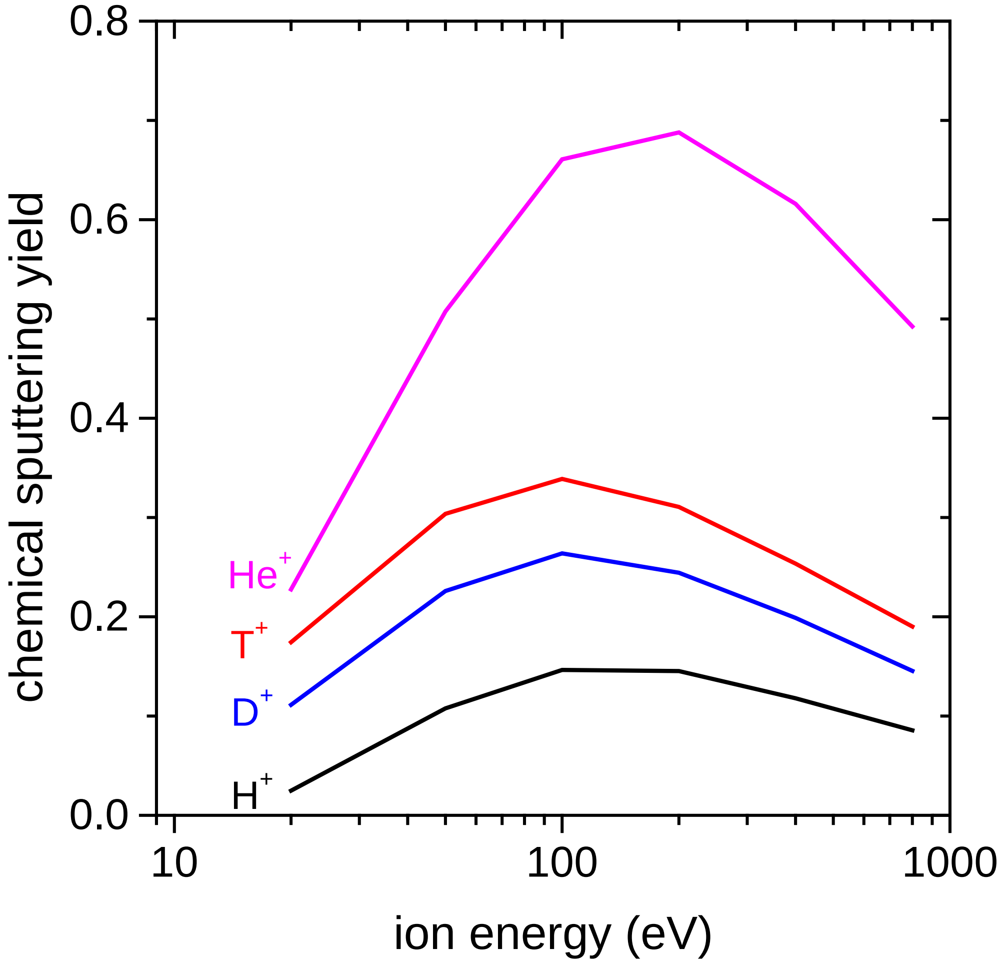
$j_H = 1.4\times10^{15}$ cm^{-2} s^{-1}, $j_{Ar+} = 3.6\times10^{12}$ cm^{-2} s^{-1}, $R = j_{H/}j_{Ar} \approx 400$

Energy dependence: Modeling results



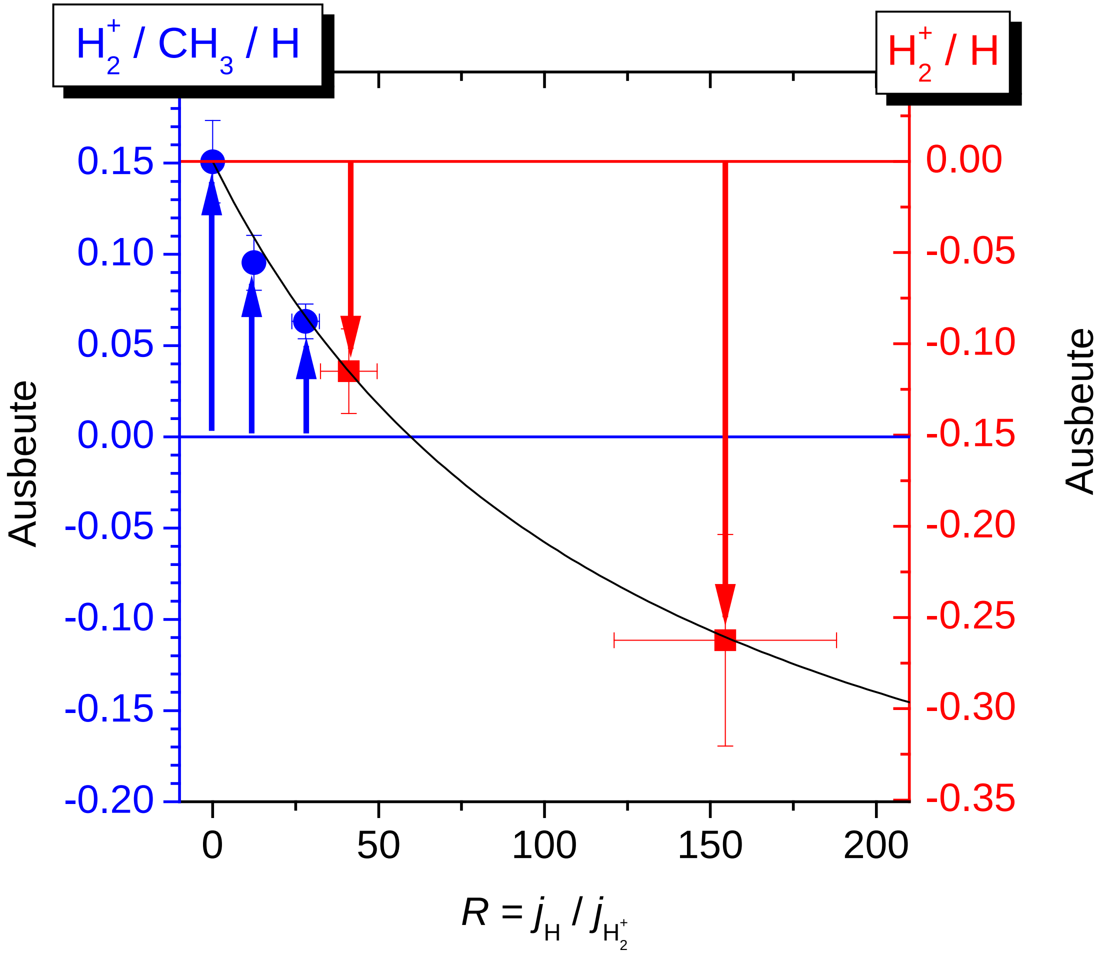
a = 0.4
R ≈ 400

Energy dependence: Modeling results



a = 0.4
R ≈ 400

Growth competition: Deposition – chem. sputtering



Growth

=

ion-induced sticking

–

chemical sputtering

here:

constant contribution from sticking

-

flux ratio dep. contribution from chemical sputtering

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, ..

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