

Chemical Sputtering of Carbon Materials due to Combined Bombardment by Ions and Atomic Hydrogen

Wolfgang Jacob, C. Hopf, M. Schlüter, and T. Schwarz-Selinger

Max-Planck-Institut für Plasmaphysik, 85748 Garching, Germany

Content:

- Physical sputtering, chemical erosion, and chemical sputtering
- The MAJESTIX experiment
- Chemical Sputtering: Initial experimental results (Ar^+)
- Quantitative model – energy dependence
- New experimental results for Ne^+ , He^+ , and N_2^+
- Summary

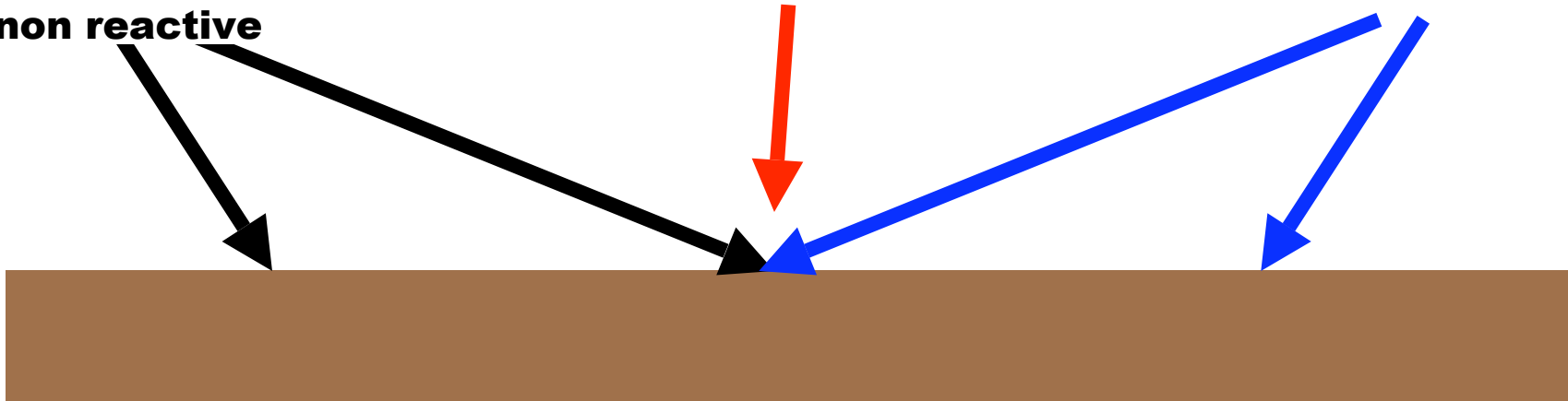
Chemical vs. physical sputtering



**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**

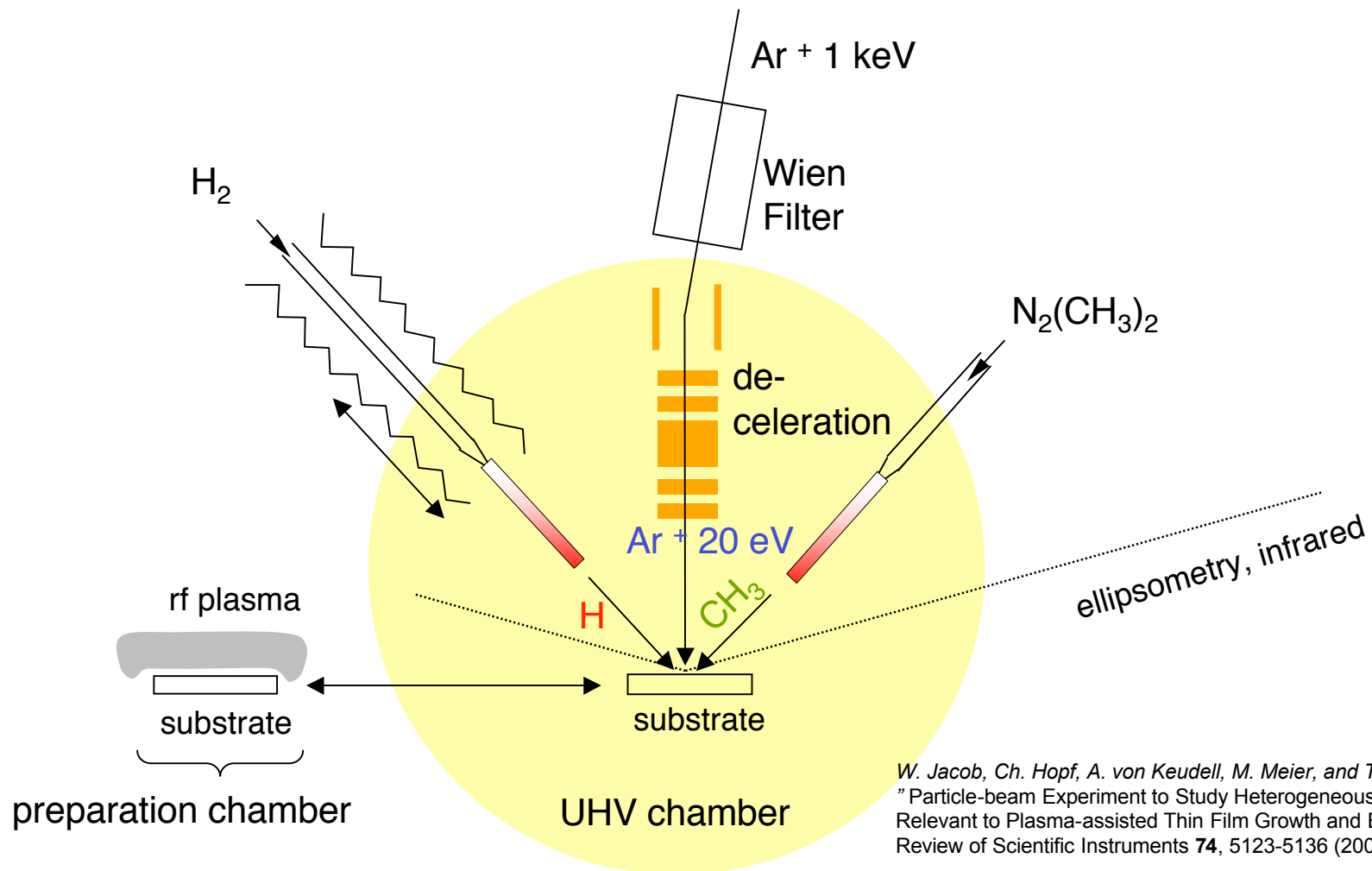
Chemical erosion

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

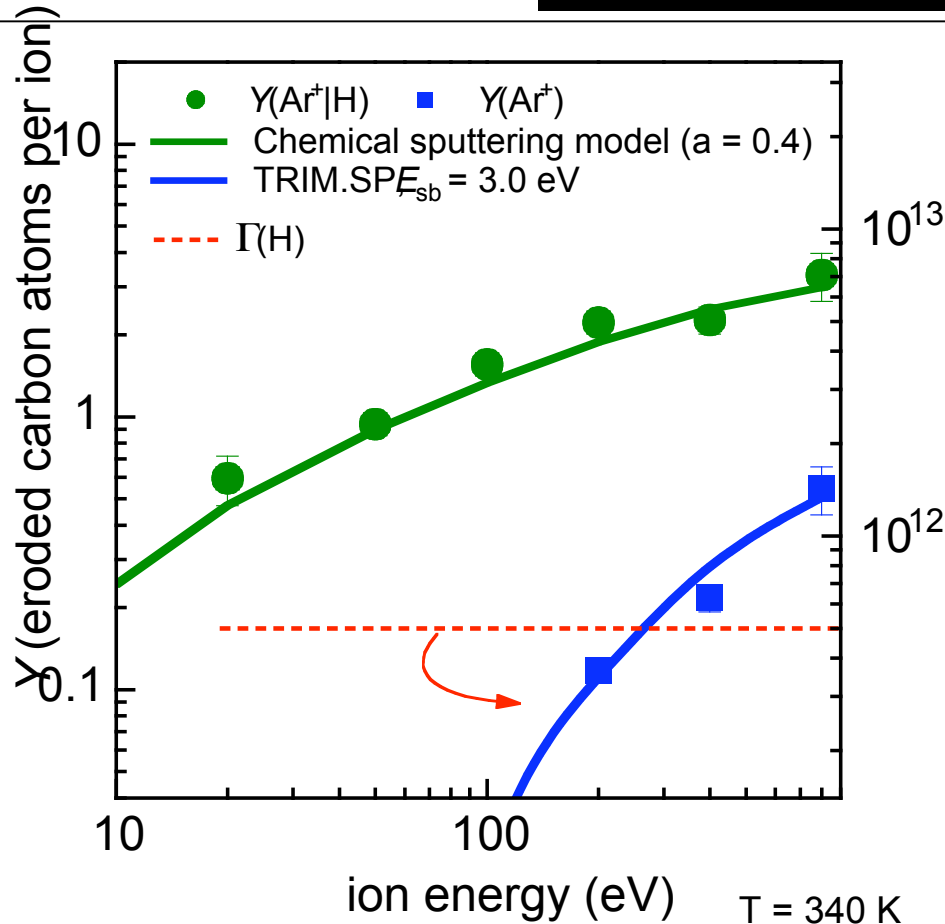
Experimental set-up



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).

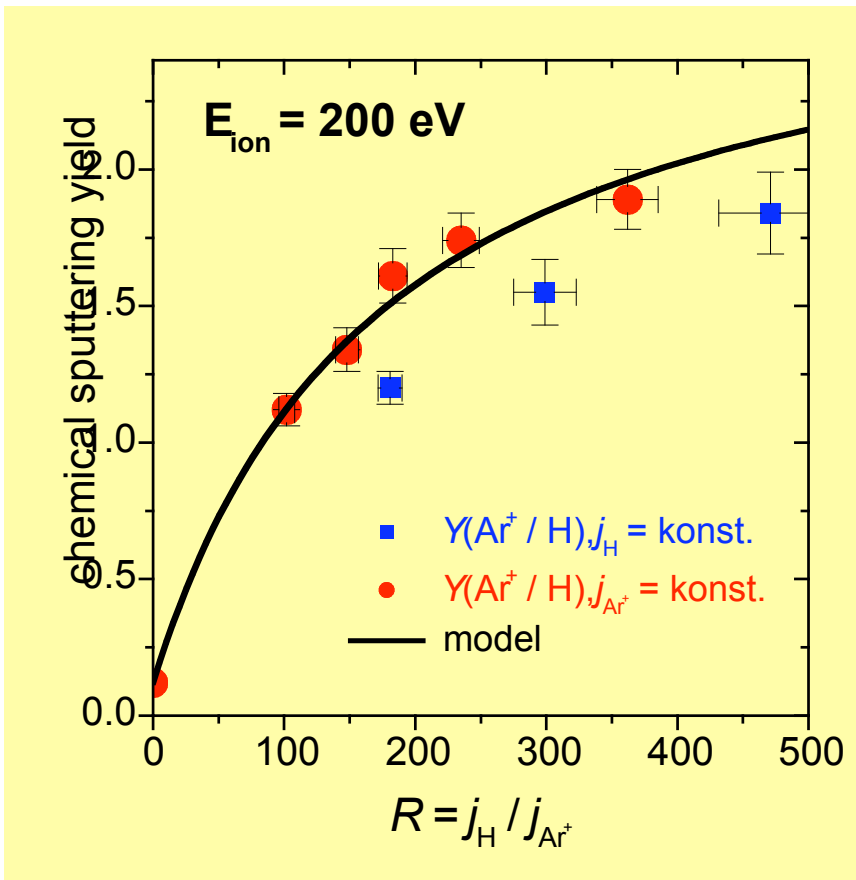


Erosion of a-C:H layers

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

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).



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

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

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

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

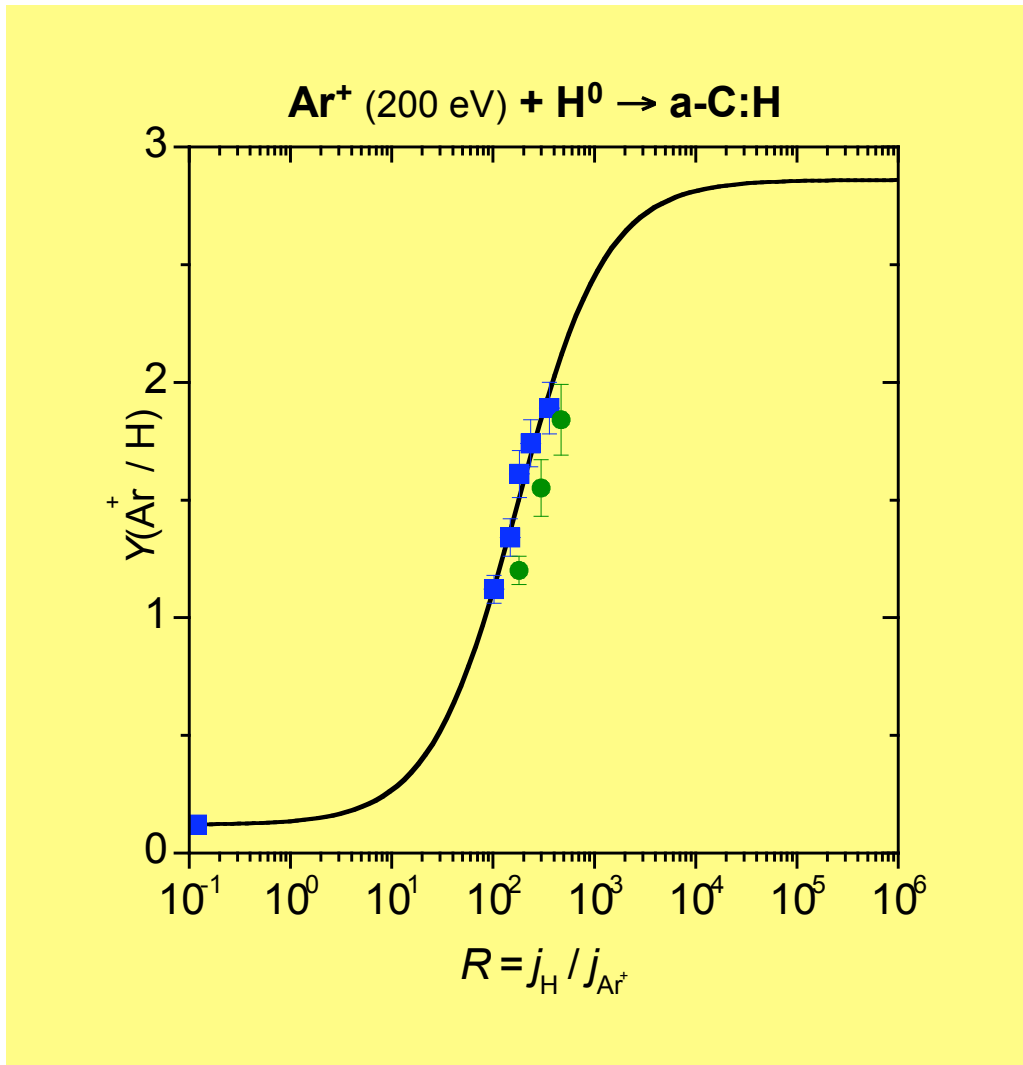
Fit parameters:

$$S = 176$$

$$Y_{\text{chem}} = 2.86$$

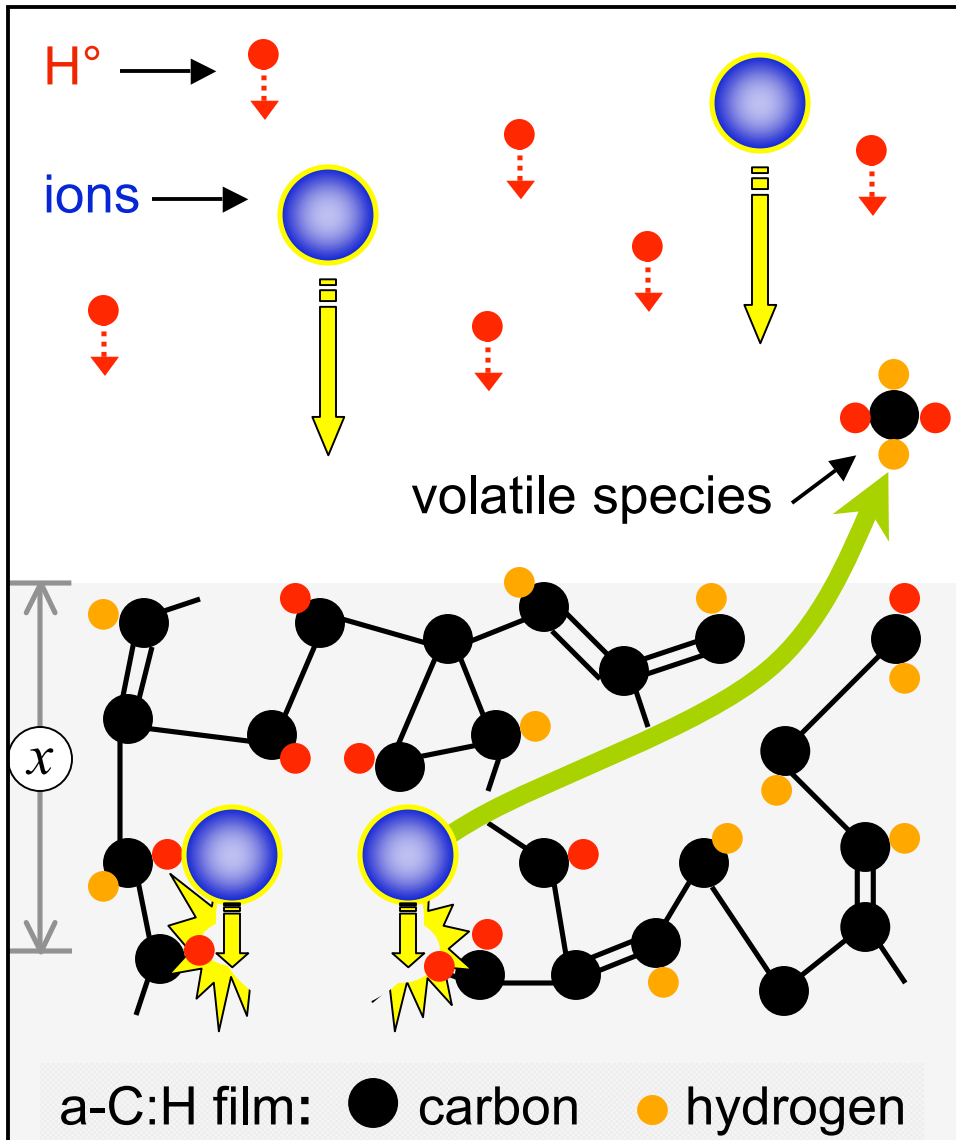
$$Y_{\text{phys}} = 0.12$$

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

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

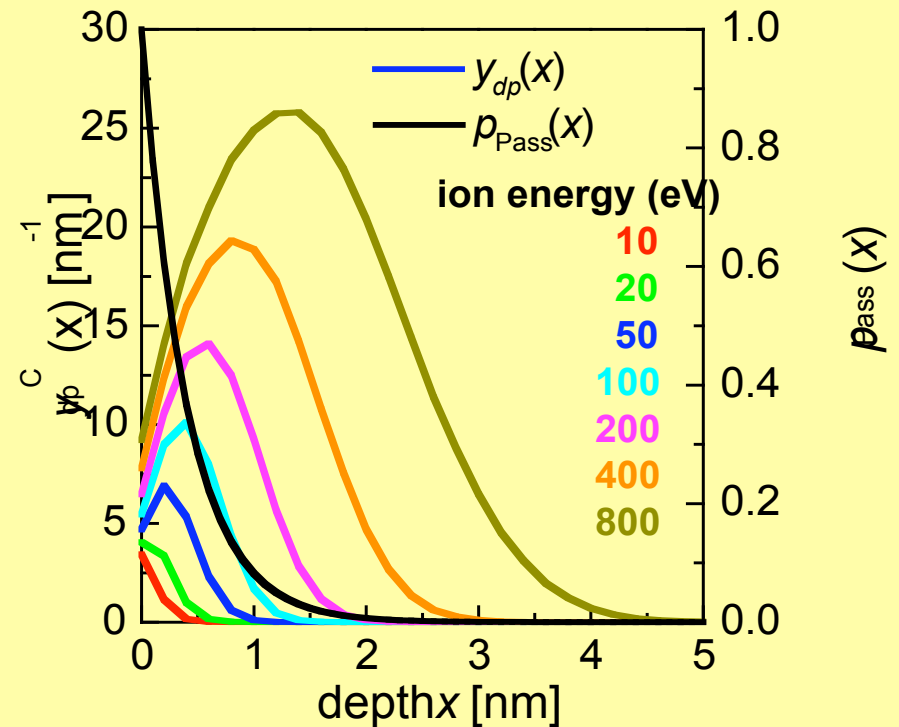
$$Y(\text{ions} | H) = a \cdot \int y_{bb}(x) \cdot e^{(-x/\lambda)} dx$$

Bond breaking events per depth interval calculated by TRIM.SP

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

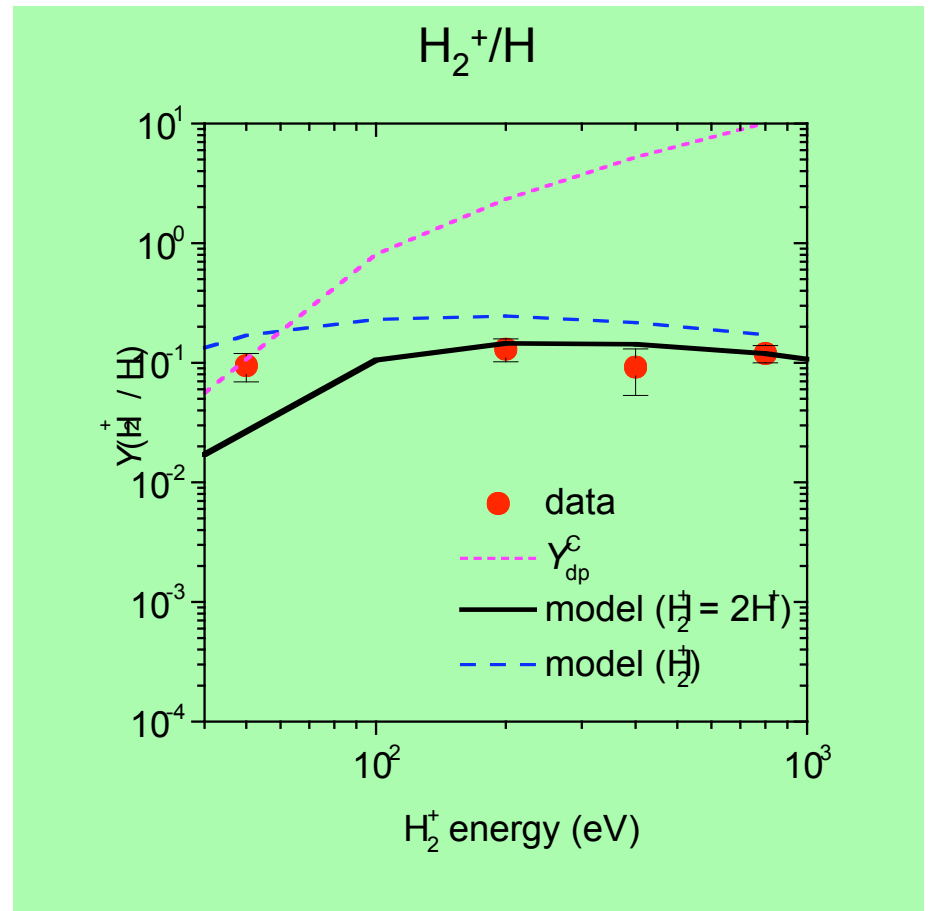
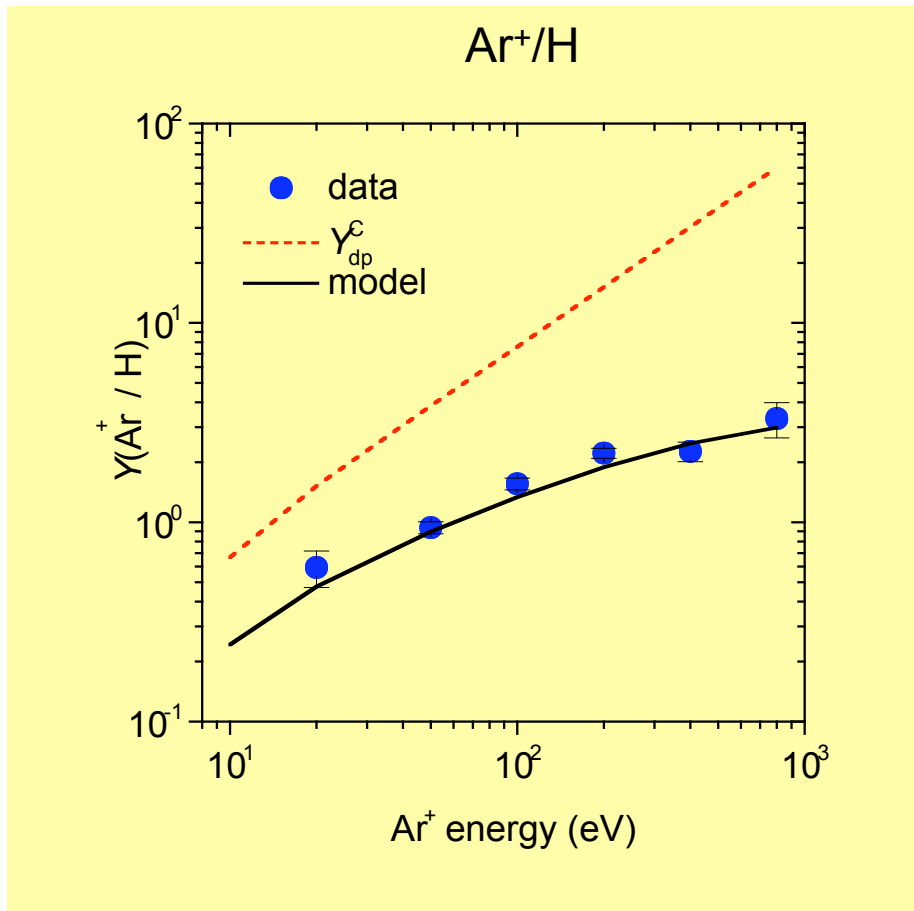
a is a fit parameter

TRIM.SP simulations for Ar ions



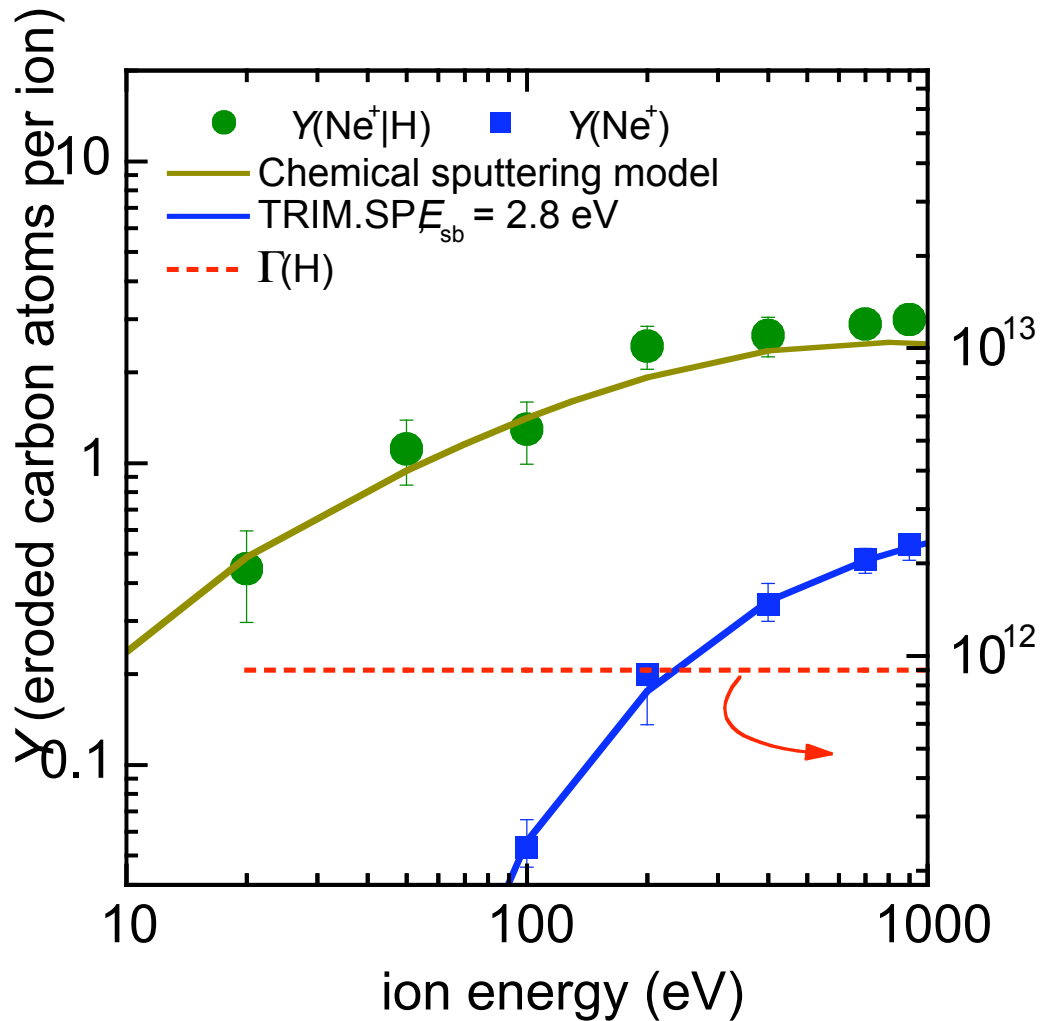
$$E_{bb}^C = 5 \text{ eV}, \lambda = 0.4 \text{ nm}$$

Energy dependence



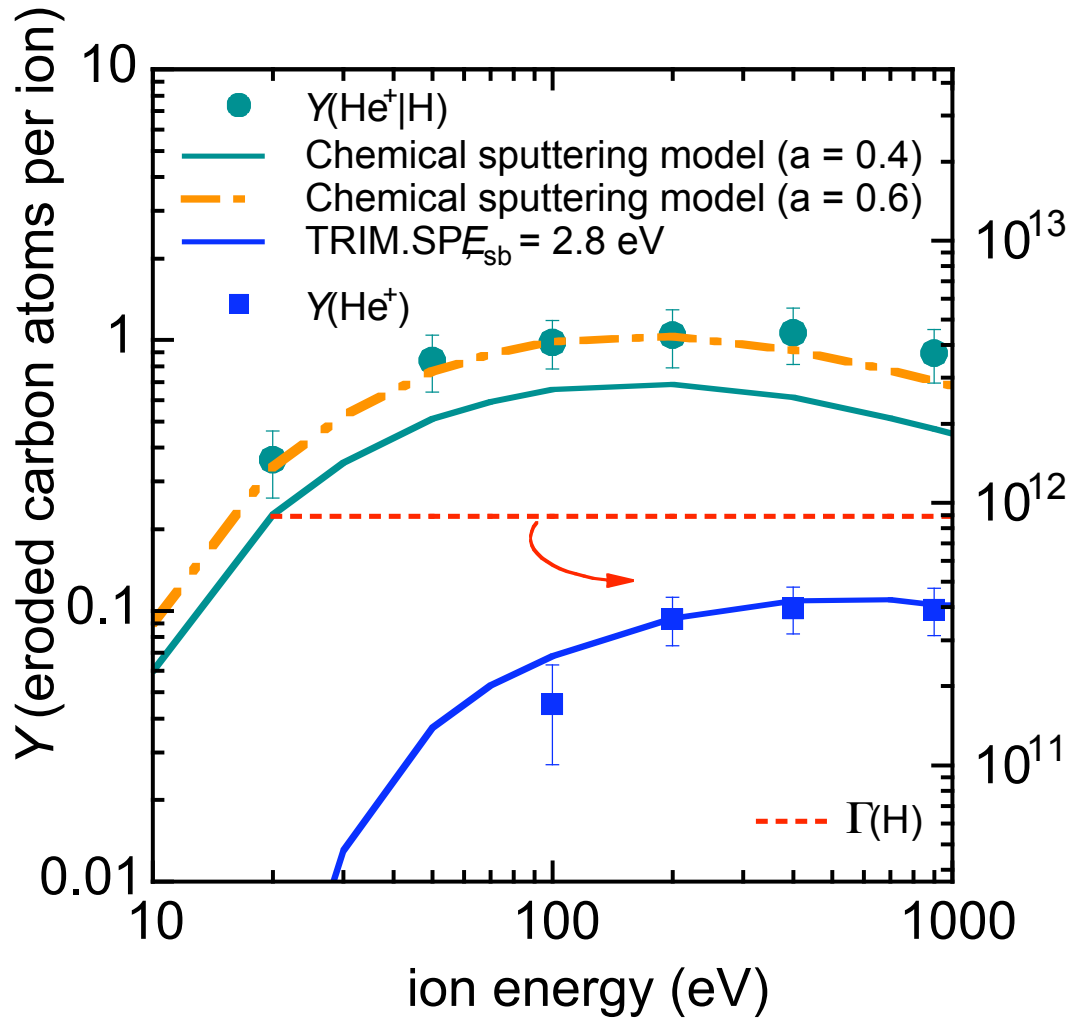
$$j_H = 1.4 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}, j_{Ar^+} = 3.6 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}, R = j_H / j_{Ar^+} \approx 400$$

New experimental results: $\text{Ne}^+ + \text{H}$

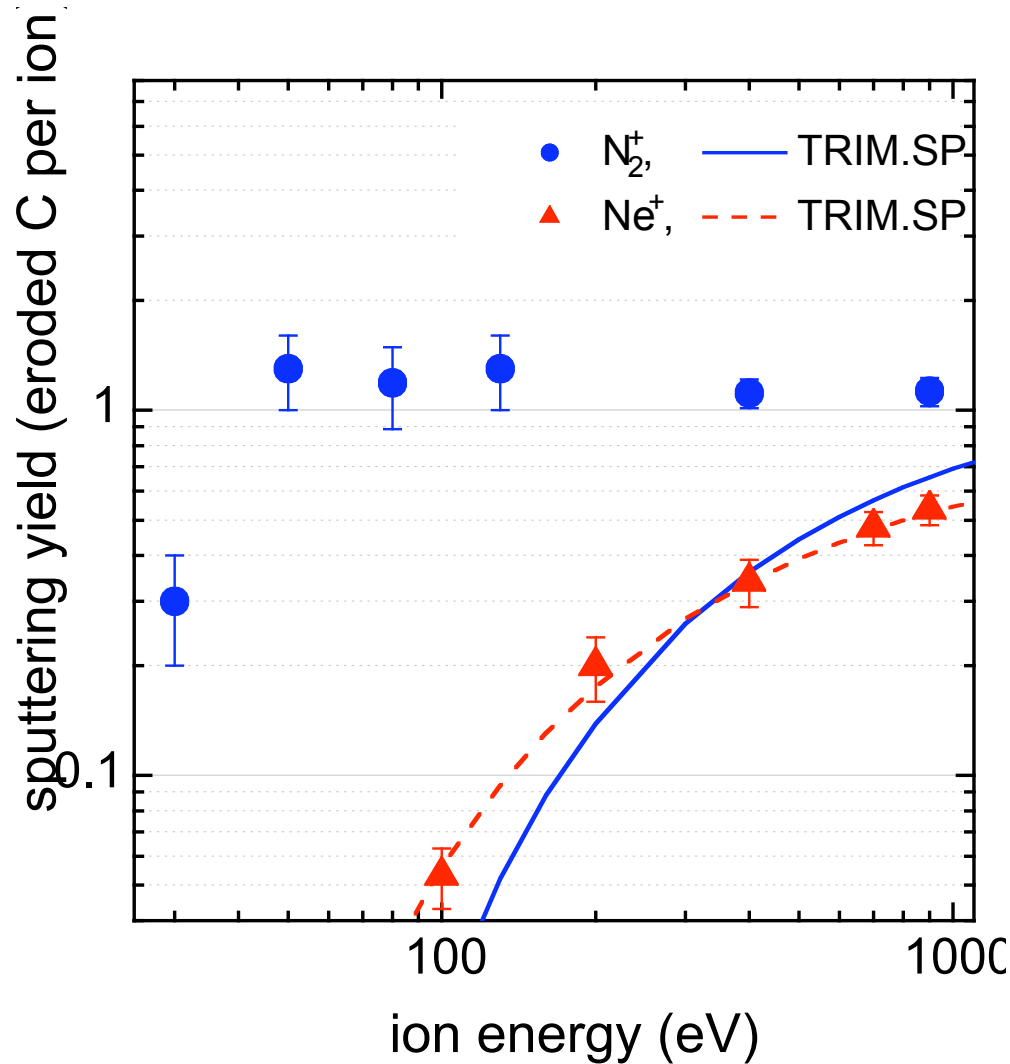


- Excellent agreement between model and data (same parameters as for Ar, i.e., $a = 0.4$)
- yield > 1 for $E_{\text{ion}} > 50 \text{ eV}$

New experimental results: He⁺ + H

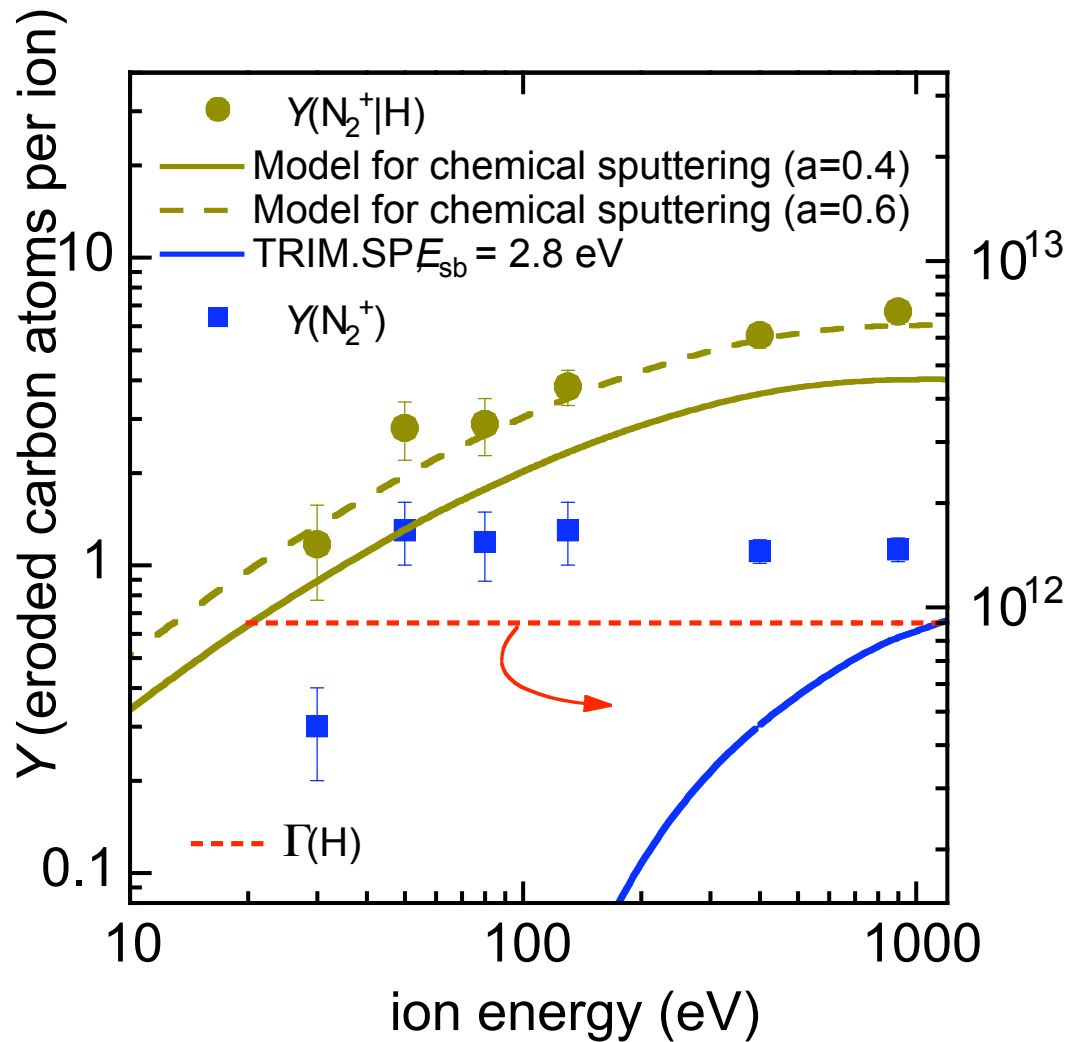


- Good fit of the energy dependence, but only for a = 0.6 (instead of 0.4)
- yield ≤ 1 in whole range



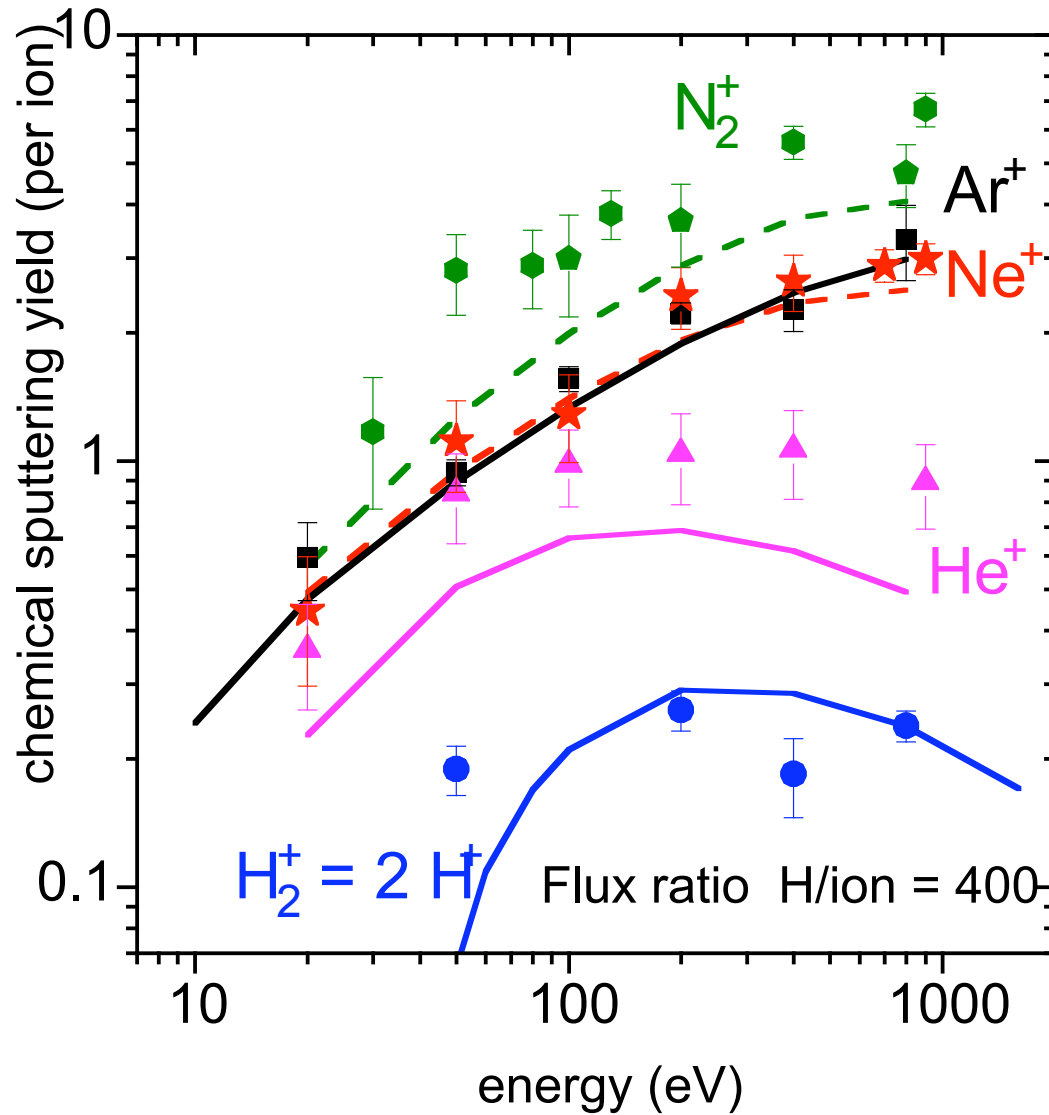
- TRIM cannot describe the results for pure N_2^+
- yield ≥ 1 for $E_{ion} > 50$ eV
- Threshold between 20 and 50 eV (TRIM ca. 100 eV)
- almost no energy dependence in range 50 to 900 eV

Chemical sputtering: $N_2^+ + H$



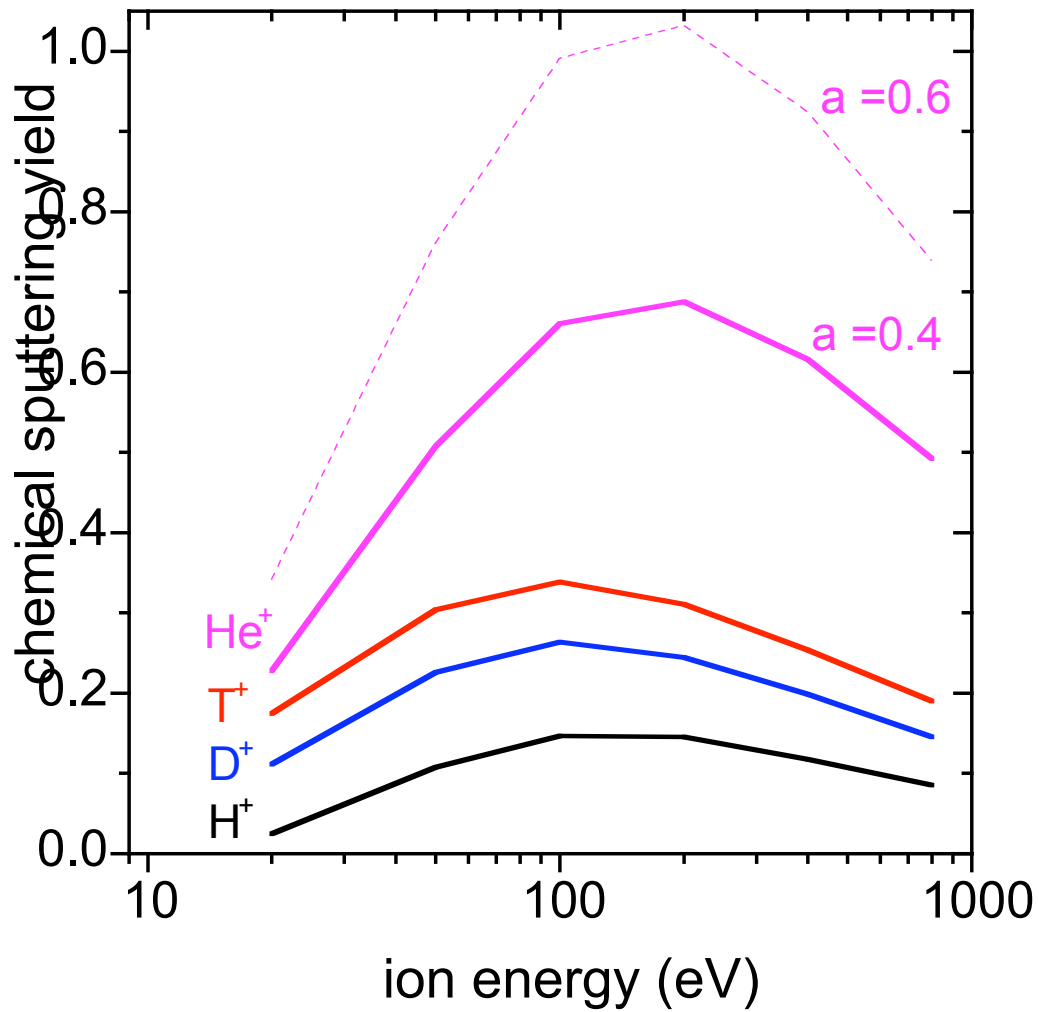
- Good fit of the energy dependence, but only for $a = 0.6$ (instead of 0.4)
- yield ≥ 1 in whole range
- highest chem. Sputt. yield of all investigates species (*good mass match to C, two atoms per ion, chemical activity*)

Chemical sputtering: Summary



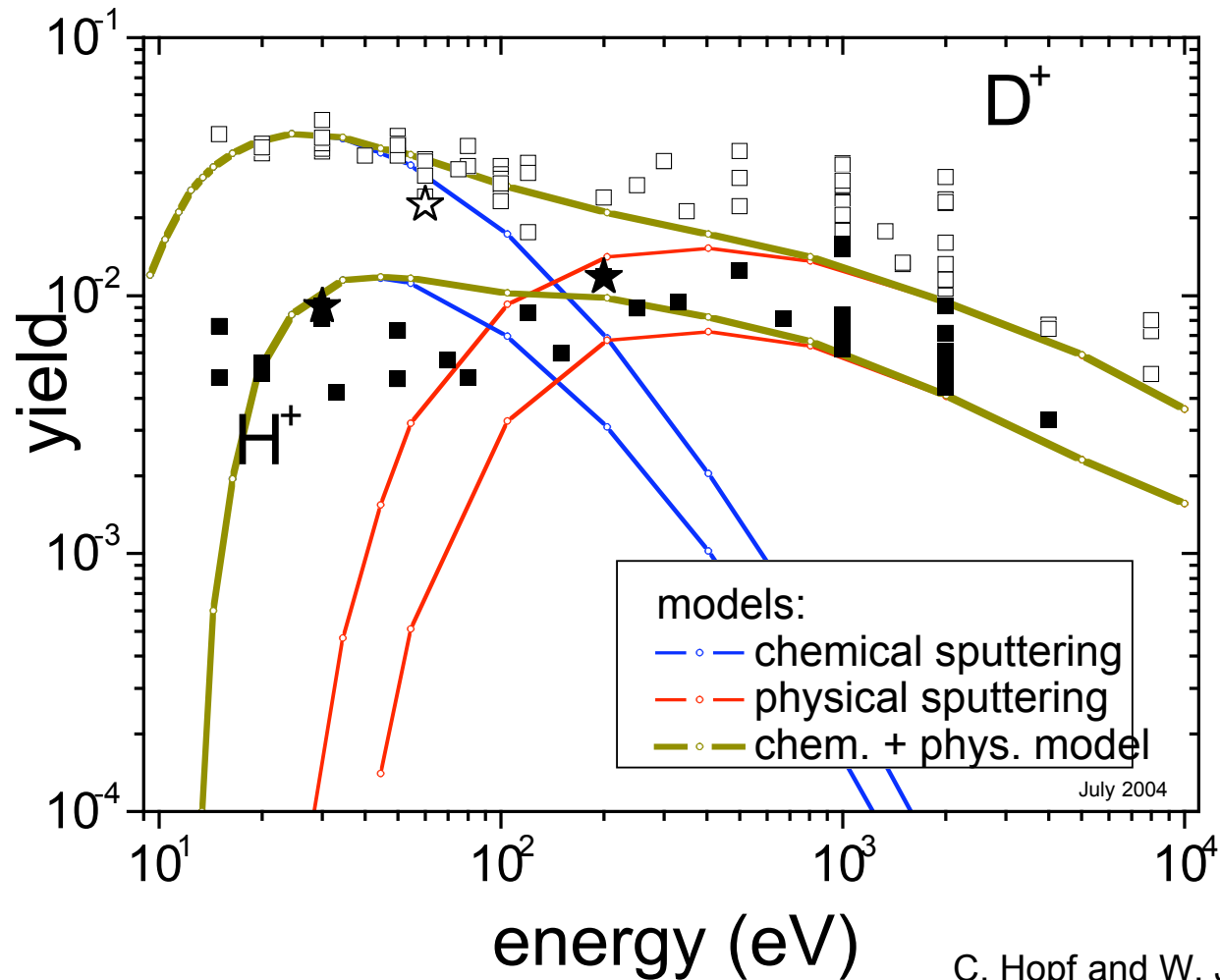
H flux density = $1.4 \times 10^{15} \text{ cm}^{-2}\text{s}^{-1}$
Ar ion flux density = $3.5 \times 10^{12} \text{ cm}^{-2}\text{s}^{-1}$

Fusion relevant species



a = 0.4
R ≈ 400

H⁺, D⁺ → graphite



Data: 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

total yield = chemical sputtering + physical sputtering

$$Y(E) = \int y_{bb}^C(x, E) n(x, E) \exp(-x / \lambda) dx + Y_{\text{phys}}(E)$$

$Y_{\text{phys}}(E)$ phys. sputtering yield

TRIM.SP

$y_{bb}^C(x, E)$ ion induced damage

$$E_{\text{sb}}^C = 7.4 \text{ eV}$$

$n(x, E)$ implanted hydrogen

$$E_{\text{bb}}^C = 5.0 \text{ eV}$$

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

$$\lambda = 0.4 \text{ nm}$$

particle-beam experiments

- *chemical sputtering*: increase of yield and lowering of threshold
- mechanistic model for *chemical sputtering*
- flux dependence (rate equation model): high H fluxes required
- energy dependence: bond breaking \times passivation
- data for Ar, Ne, He, and N₂
- predictions for other ions, e.g. H, D, and T
- N₂⁺ alone results in *chemical sputtering* of a-C:H layers
- N₂⁺ + H shows very high *chemical sputtering* yield

The end

Collaborators:

Christian Hopf

Achim von Keudell

Michael Schlüter

Thomas Schwarz-Selinger