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

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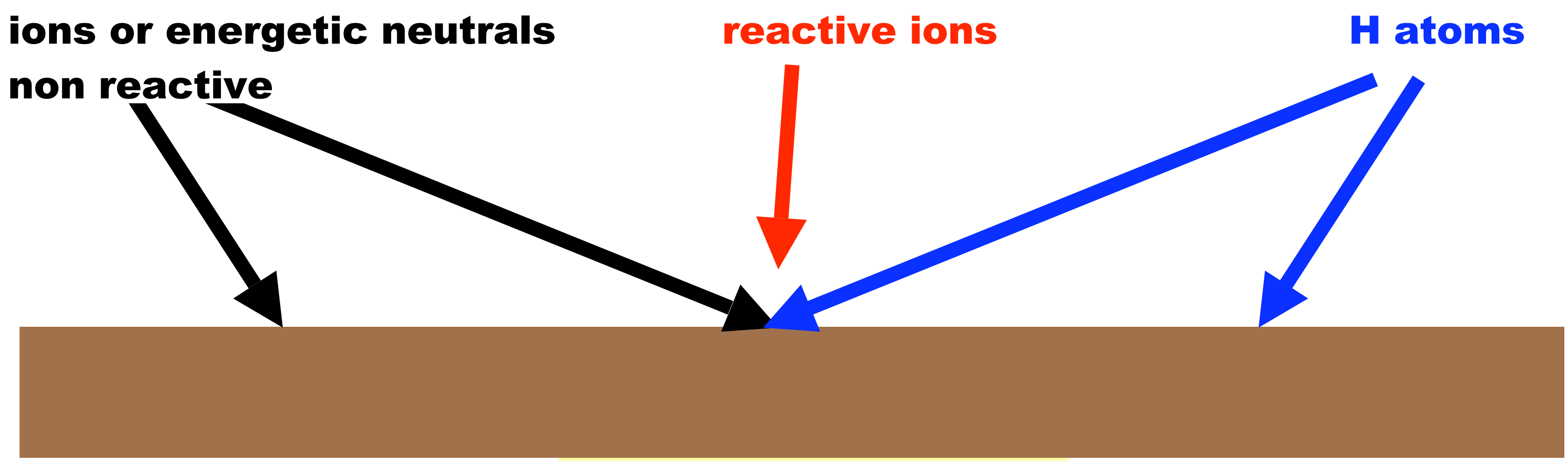
Content:

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

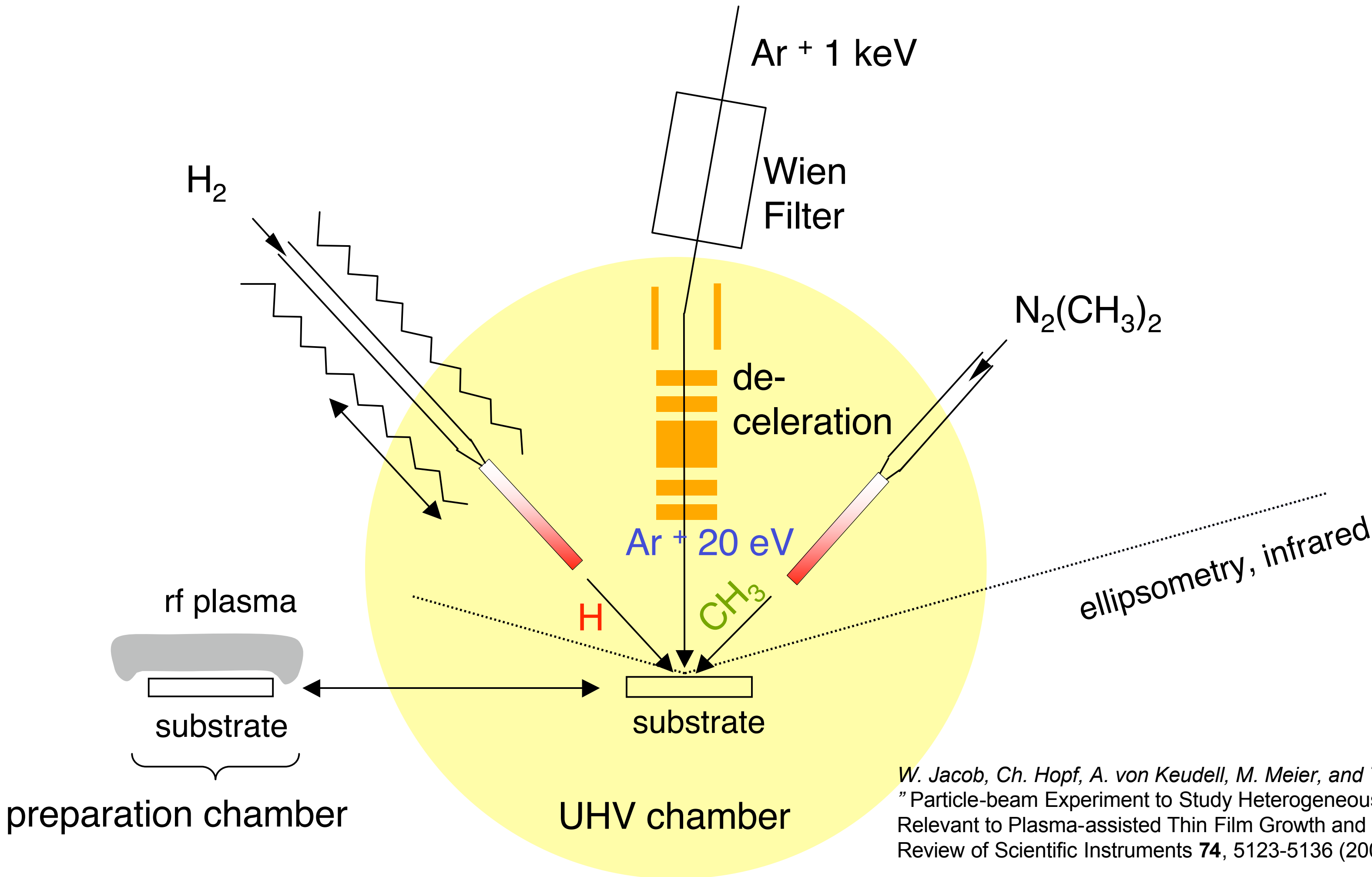
- **ions + neutrals**
- **energy dependence**
- **T dependence**
- **very low threshold energy**
- **isotope effect**
- **ion-to-neutral ratio dep.**
- **high erosion yield**

Chemical erosion

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

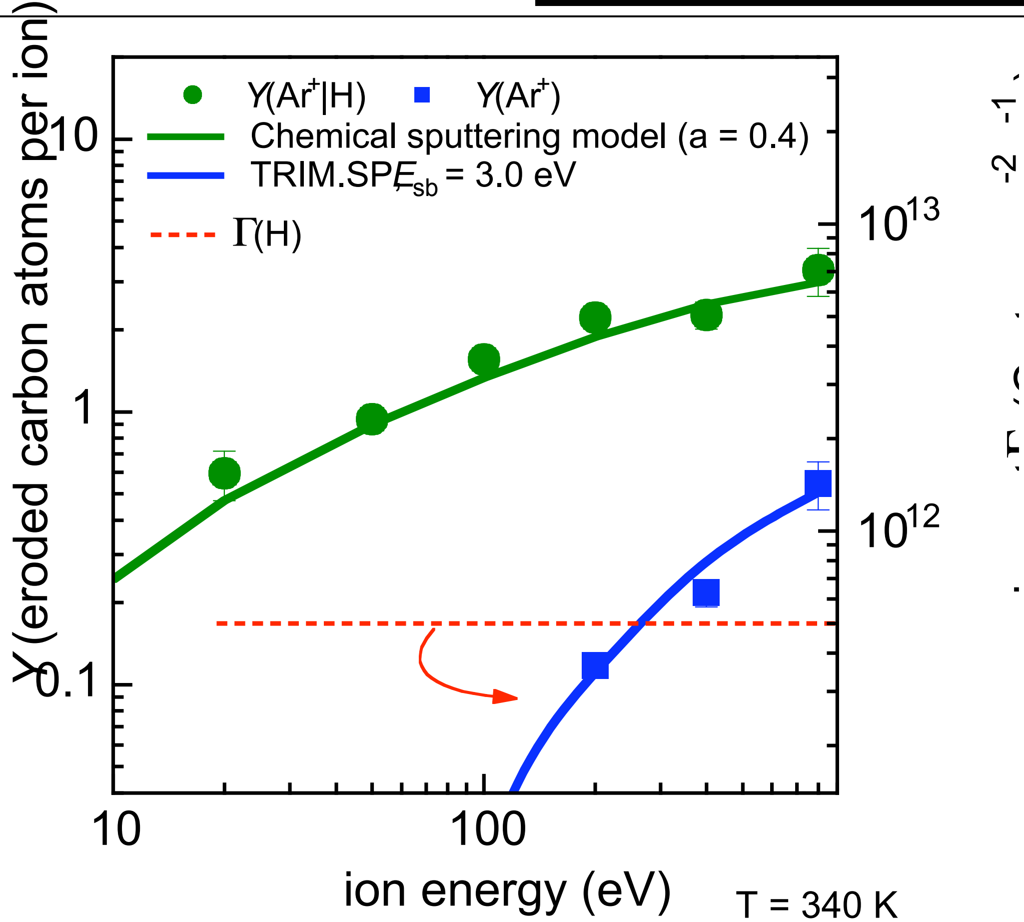
Experimental set-up

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).

Chemical Sputtering



Erosion of a-C:H layers

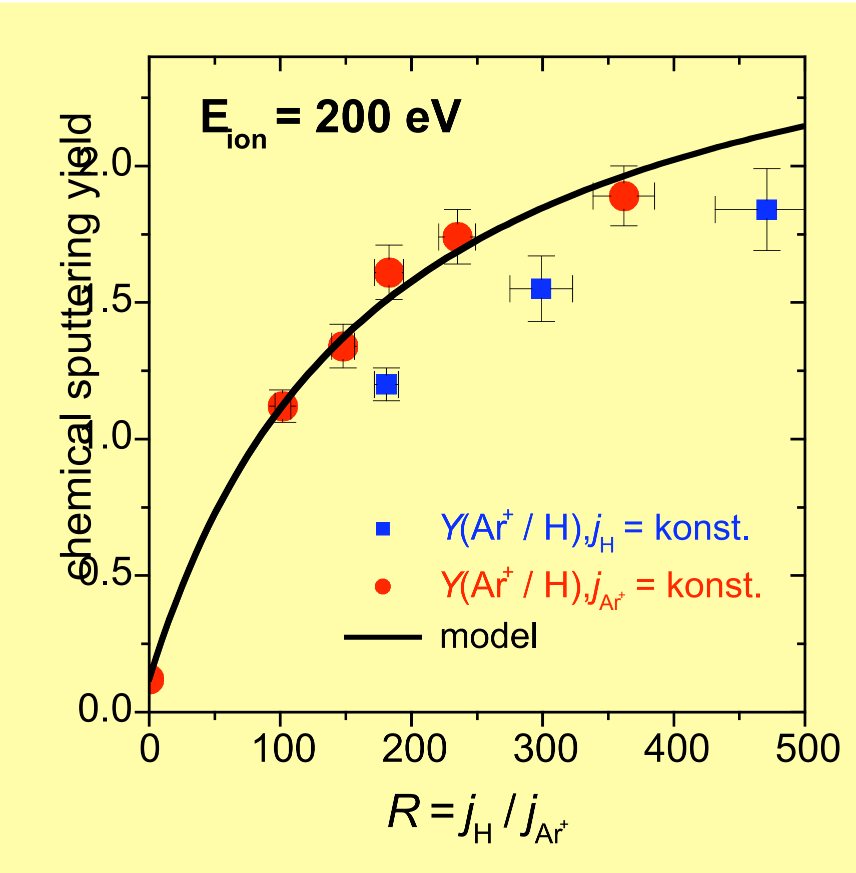
comparison of simple physical sputtering (blue symbols) due to Ar ions
with
erosion due to simultaneous interaction of H and Ar^+ (green symbols).

- 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).*

Ar^+|H flux dependence



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

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

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

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

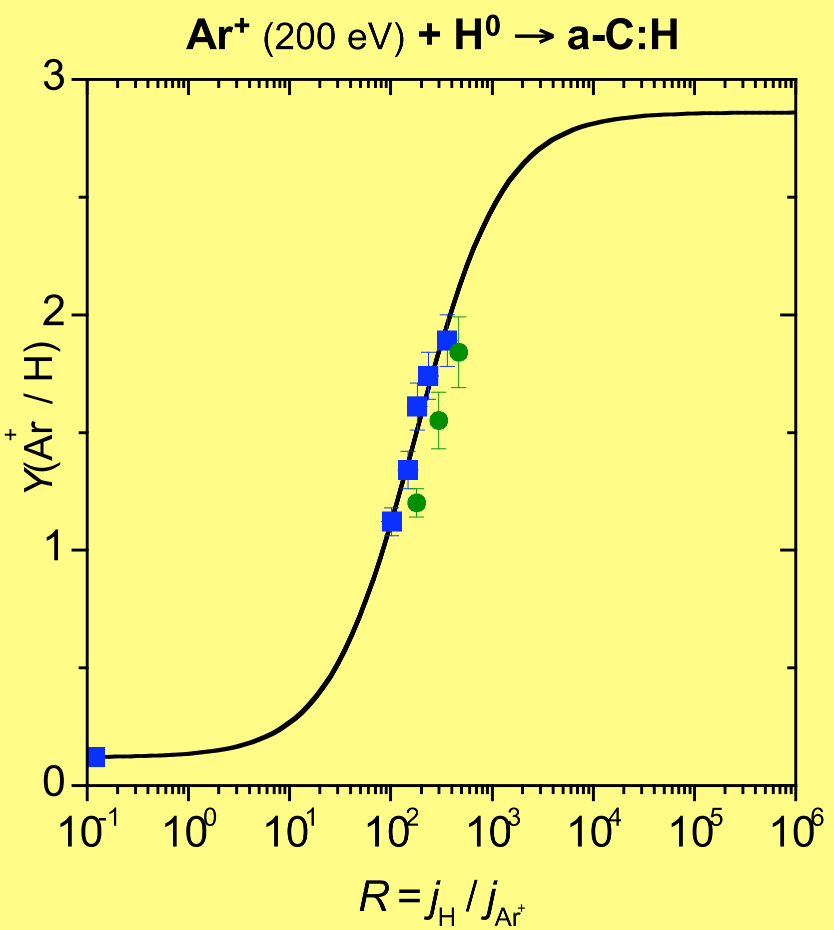
Fit parameters:

$S = 176$

$Y_{chem} = 2.86$

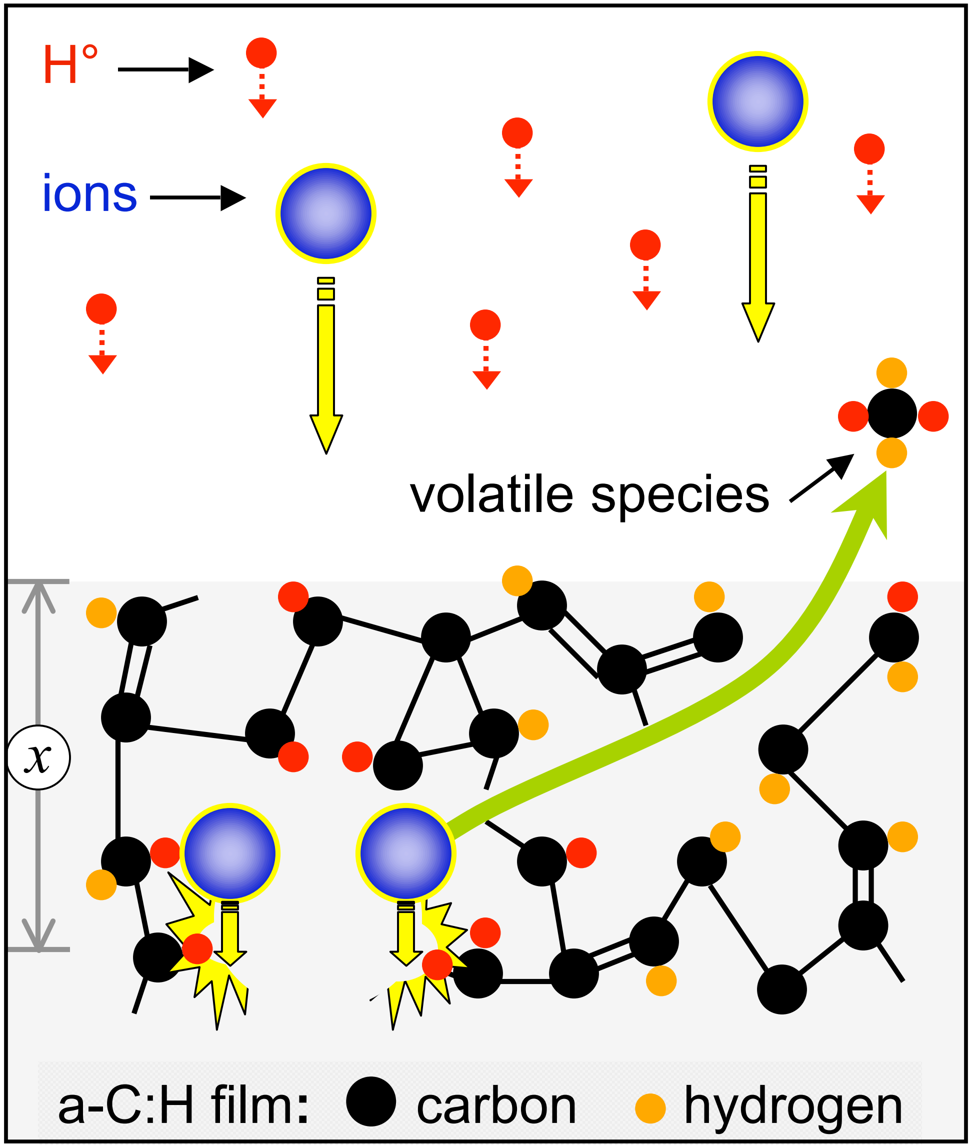
$Y_{phys} = 0.12$

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

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

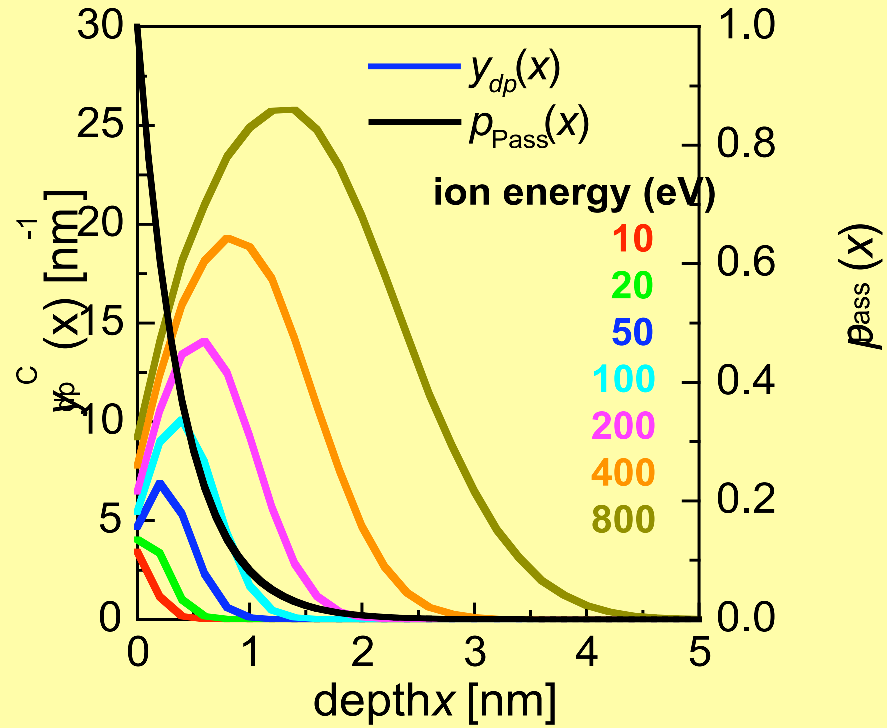
$$Y(ions\,|\,H) = a \cdot \int y_{bb}(x) \cdot e^{(-x/\lambda)}\,dx$$

Bond breaking events per depth interval calculated by TRIM.SP

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

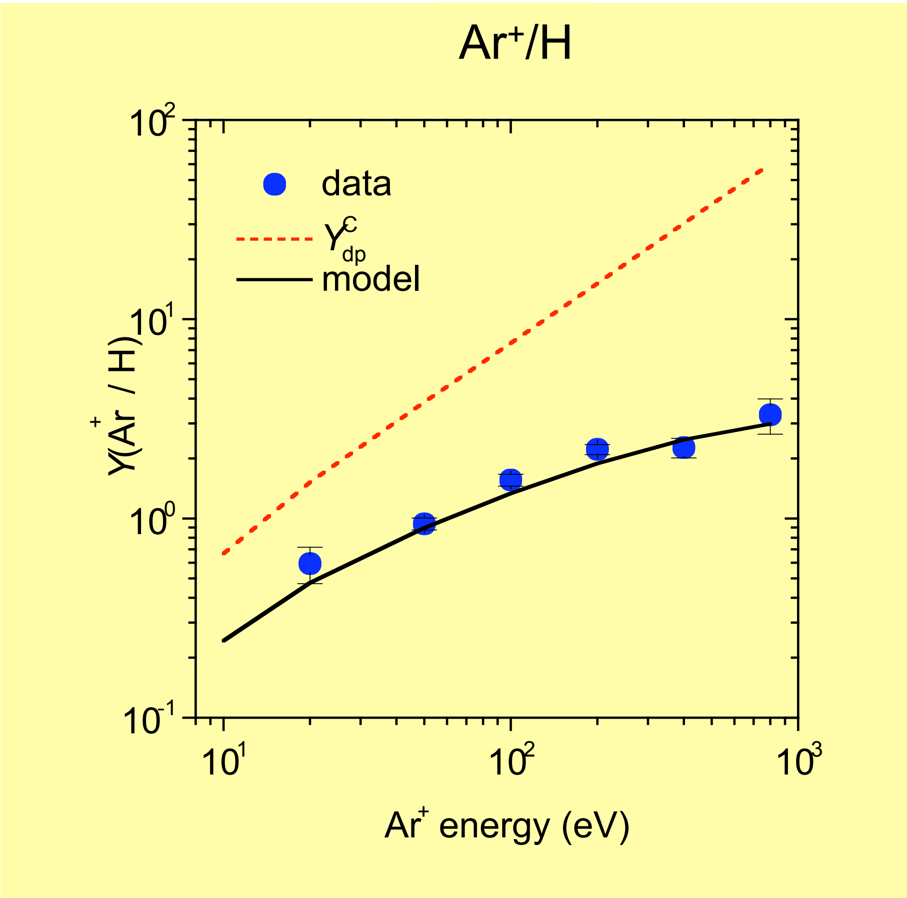
a is a fit parameter

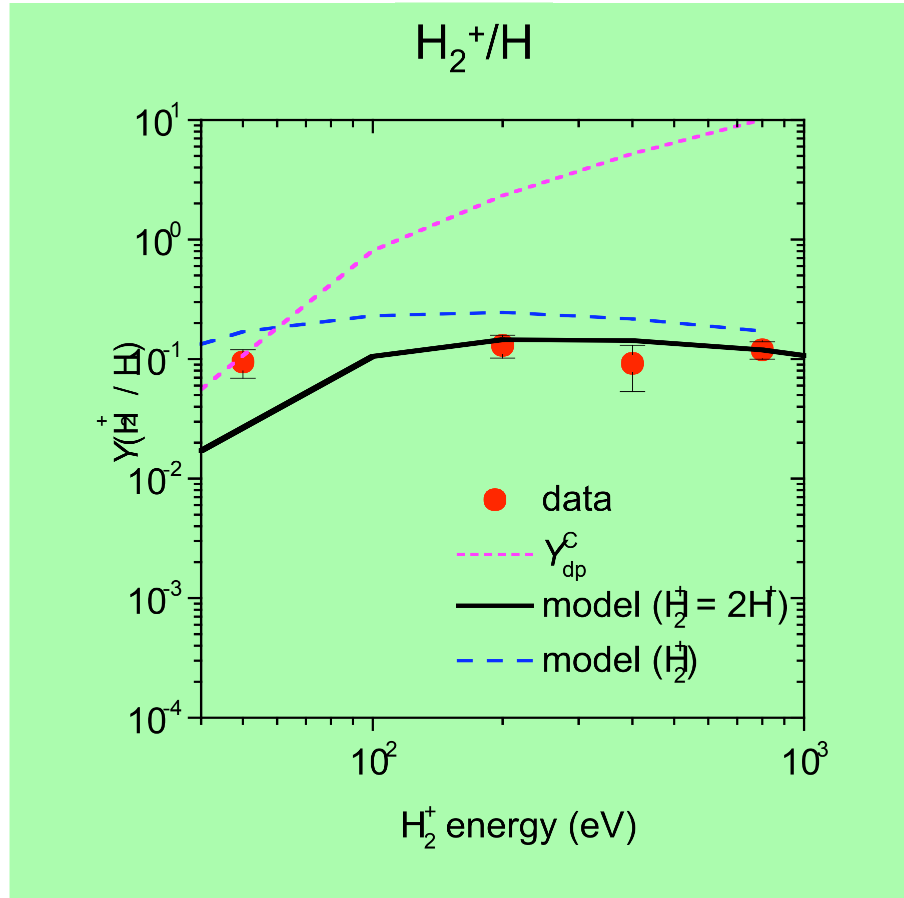
TRIM.SP simulations for Ar ions



$E_{bb}{}^{C}$ = 5 eV, λ = 0.4 nm

Energy dependence



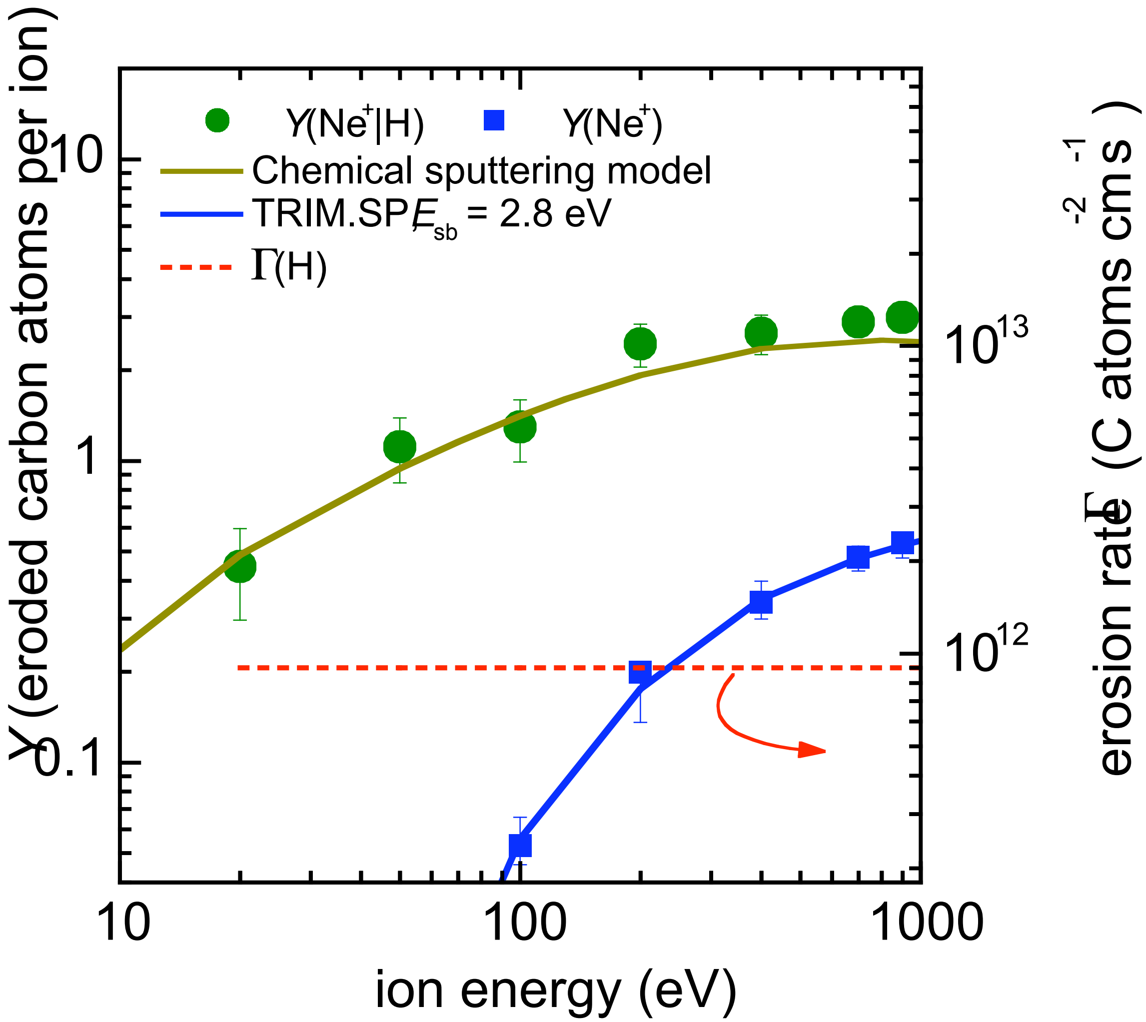


a = 0.4

a = 0.4

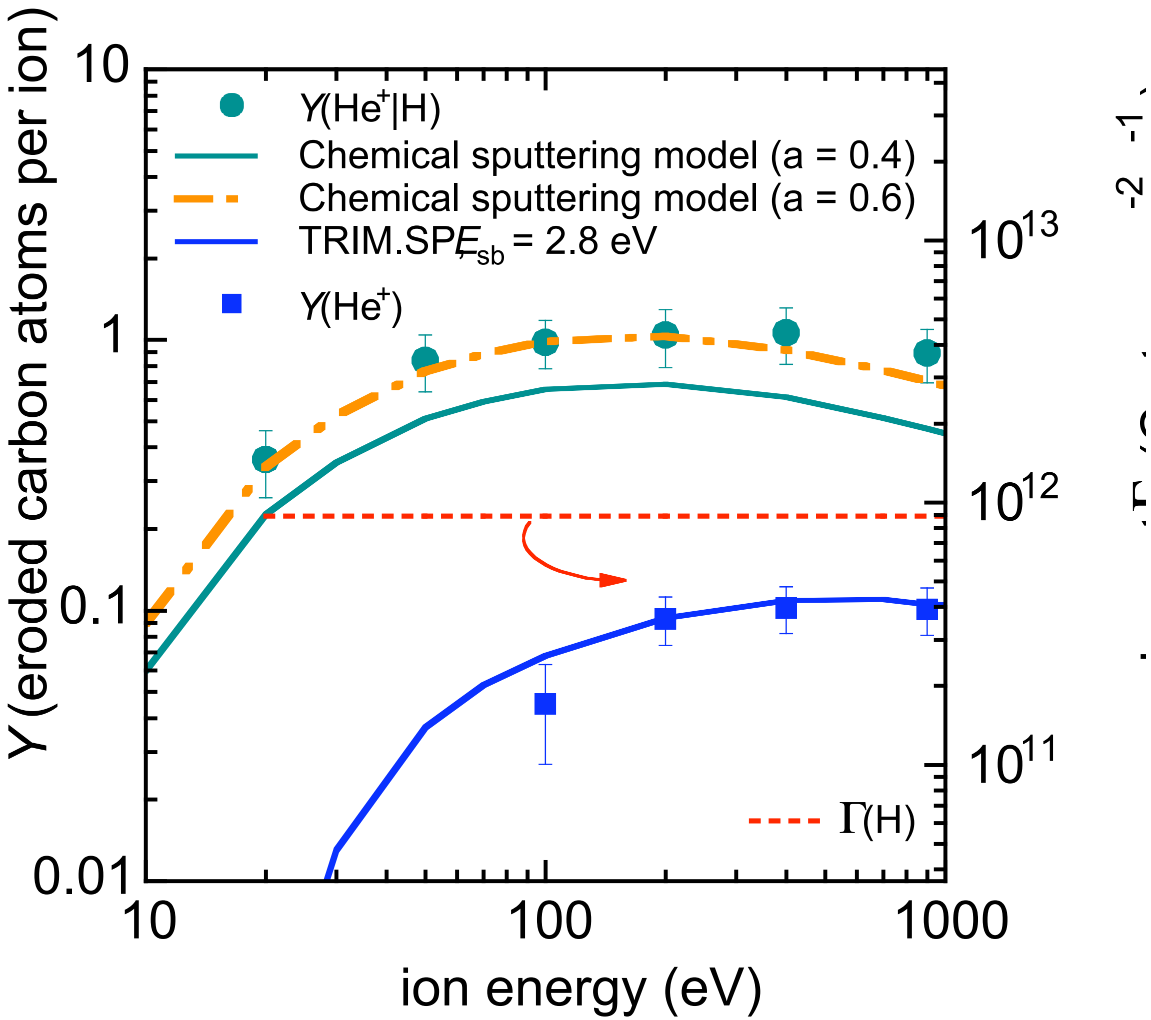
$j_H = 1.4\times10^{15}$ cm^{-2} s^{-1}, $j_{Ar+} = 3.6\times10^{12}$ cm^{-2} s^{-1}, $R = j_{H/} j_{Ar} \approx 400$

New experimental results: $Ne^+ + H$



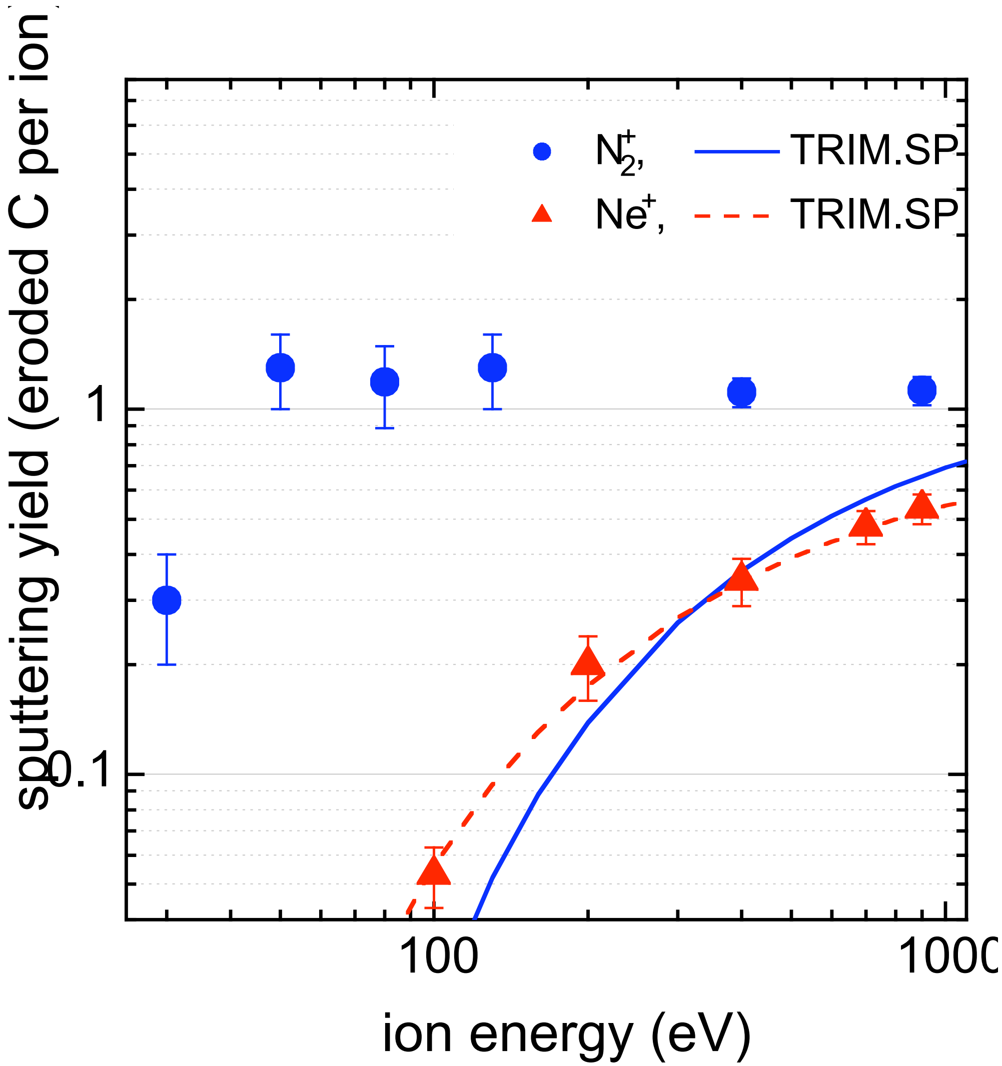
- Excellent agreement between model and data (same parameters as for Ar, i.e., a = 0.4))
- yield > 1 for E_{ion} >50 eV

New experimental results: $He^+ + H$



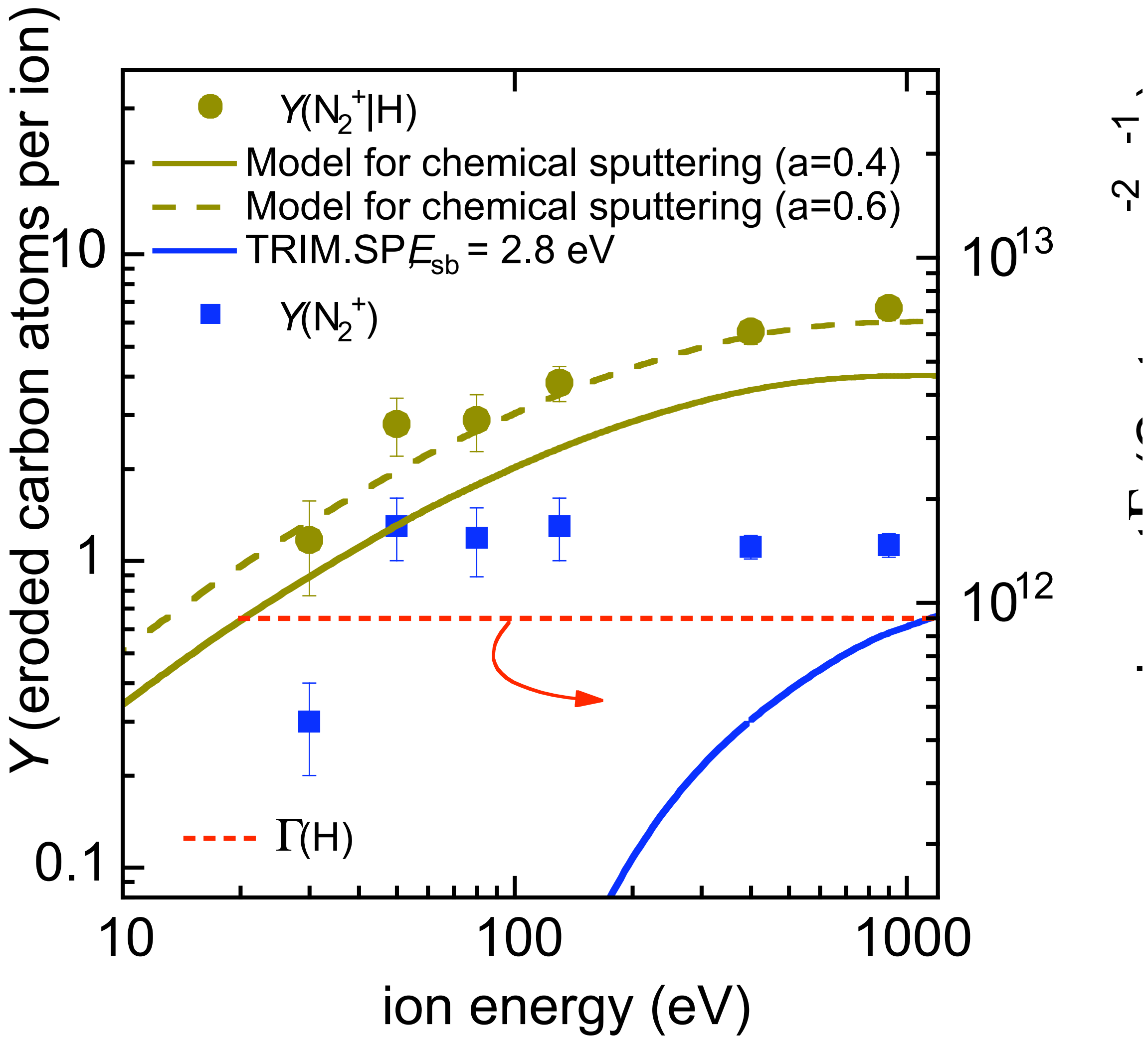
- Good fit of the energy dependence,
  but only for a = 0.6
  (instead of 0.4)
- yield ≤ 1 in whole range

Chemical sputtering by N_2^+



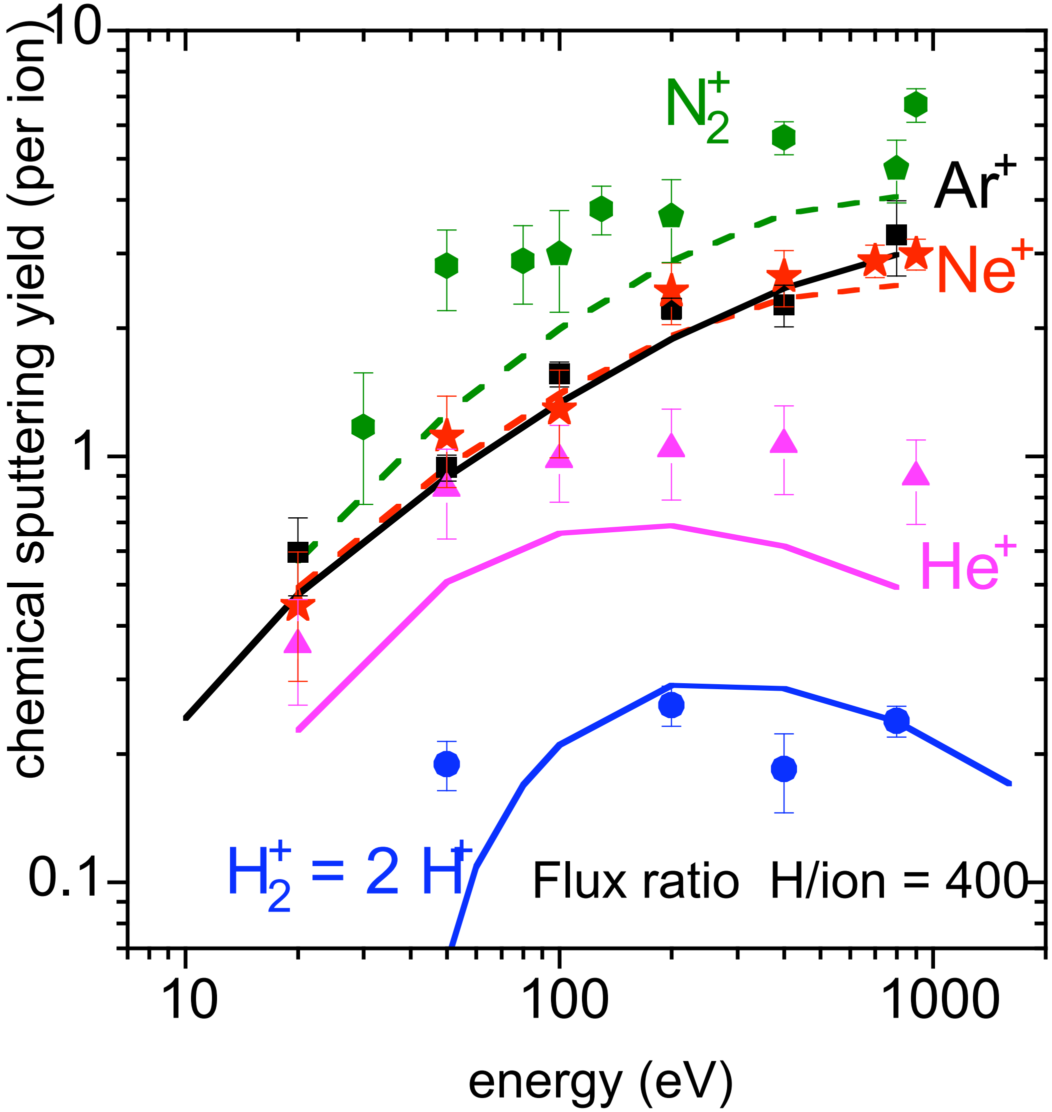
- TRIM cannot describe the results for pure N_2^+
- yield ≥ 1 for E_{ion} > 50 eV
- Threshold between 20 and 50 eV (TRIM ca. 100 eV)
- almost no energy dependence in range 50 to 900 eV

Chemical sputtering: N_2^+ + H



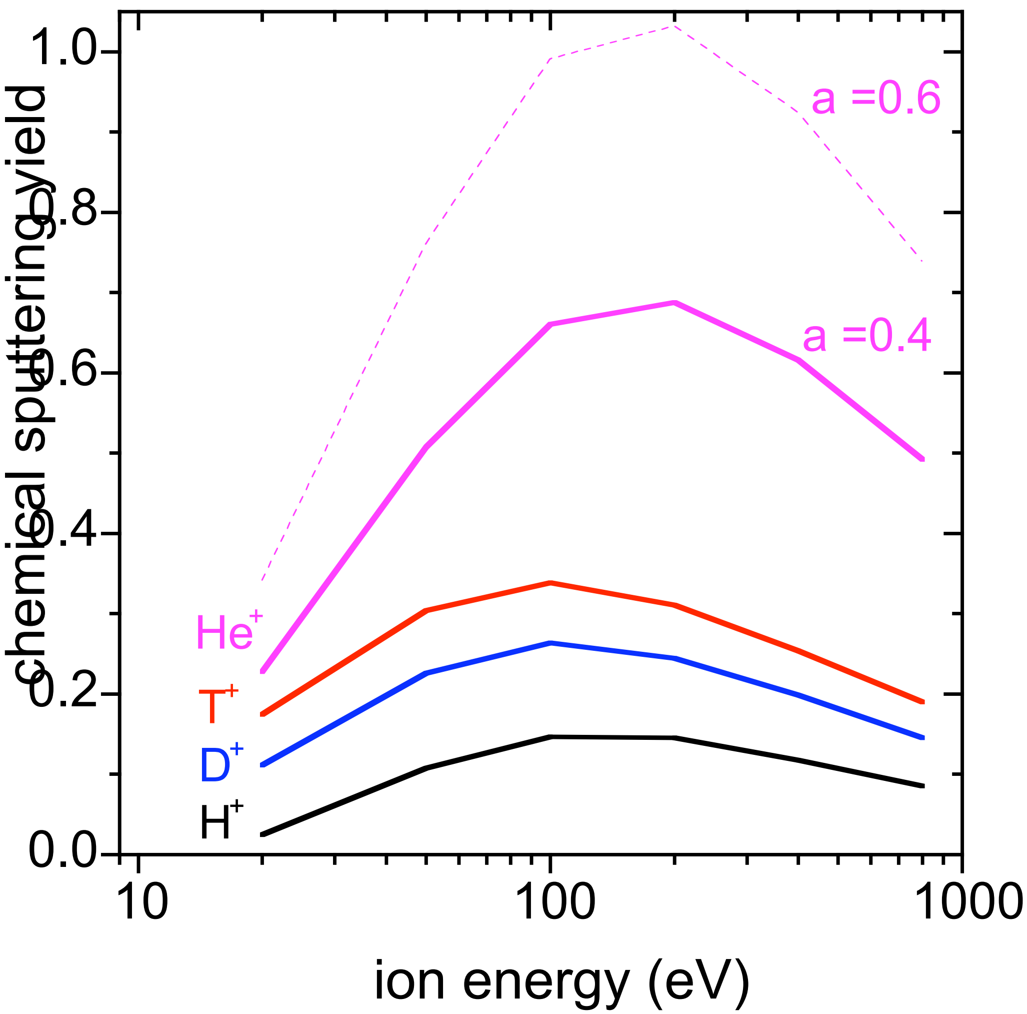
- Good fit of the energy dependence, but only for a = 0.6 (instead of 0.4)
- yield ≥ 1 in whole range
- highest chem. Sputt. yield of all investigates species *(good mass match to C, two atoms per ion, chemical activity)*

Chemical sputtering: Summary



H flux density = 1.4×10^{15} cm^{-2}s^{-1}
Ar ion flux density = 3.5×10^{12} cm^{-2}s^{-1}

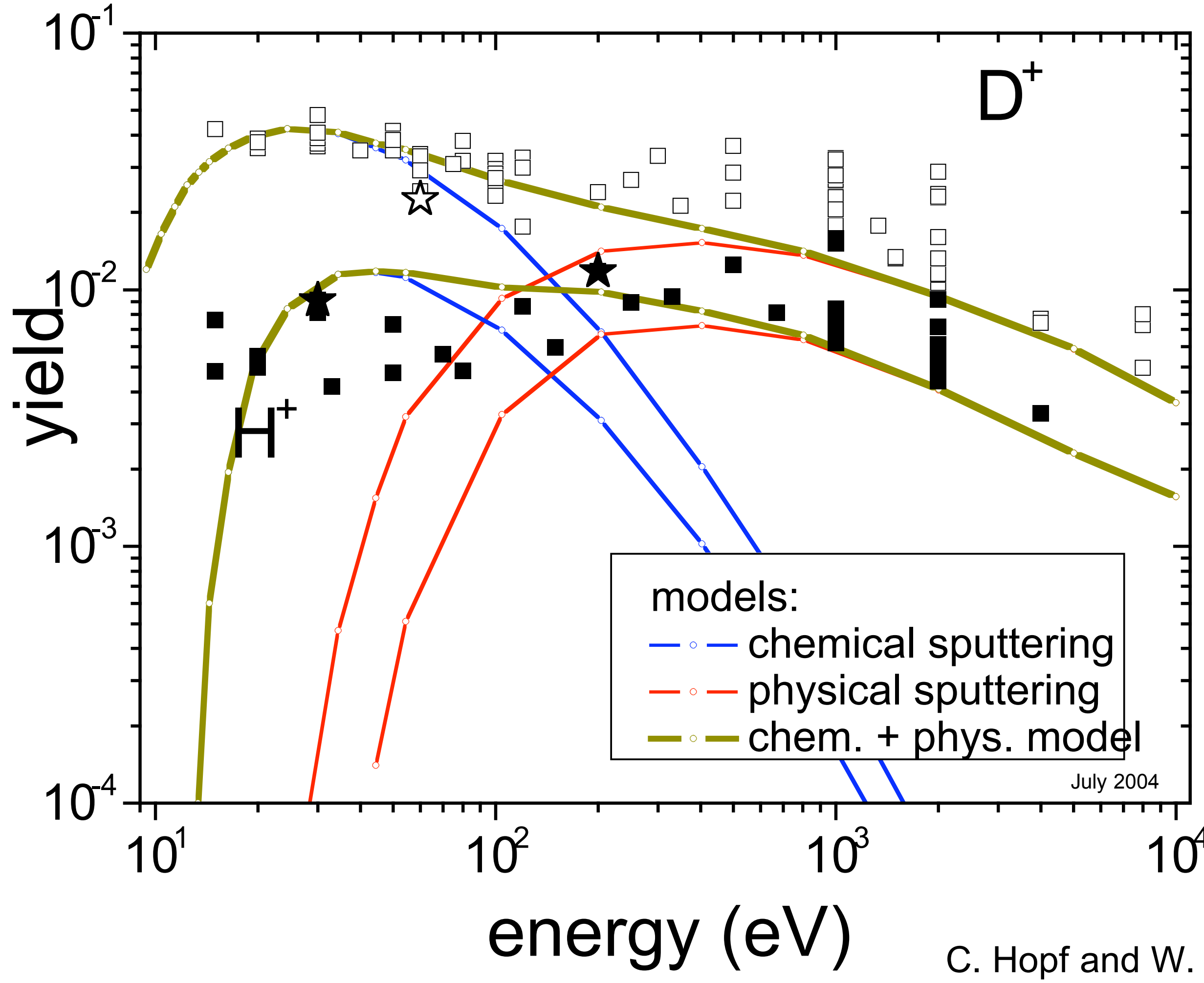
Fusion relevant species



a = 0.4
R ≈ 400

Chemical sputtering with reactive ions

H^+, D^+ → graphite



C. Hopf and W. Jacob, submitted

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

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

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

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

Summary

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 × passivation
- data for Ar, Ne, He, and N_2
- predictions for other ions, e.g. H, D, and T
- N_2^+ alone results in *chemical sputtering* of a-C:H layers
- N_2^+ + H shows very high *chemical sputtering* yield

The end

Collaborators:

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