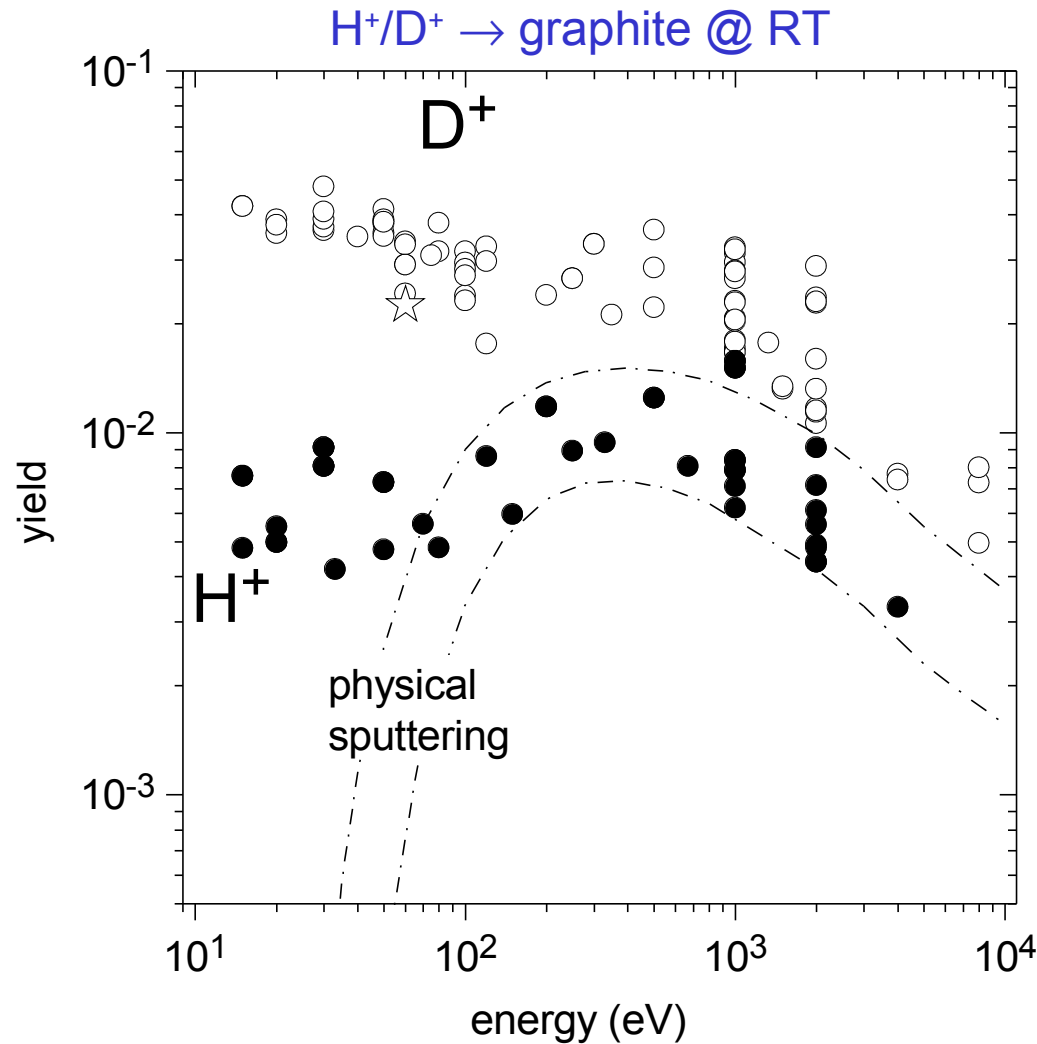


Chemical sputtering of C with atomic H: Synergetic effects

Christian Hopf, Wolfgang Jacob, Michael Schlueter,
P. N. Maya, and Udo von Toussaint

Motivation



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

Bombardment of C with energetic hydrogen:

Erosion rates @ low $E >$ physical sputtering
 and
 erosion even below threshold of physical sputtering

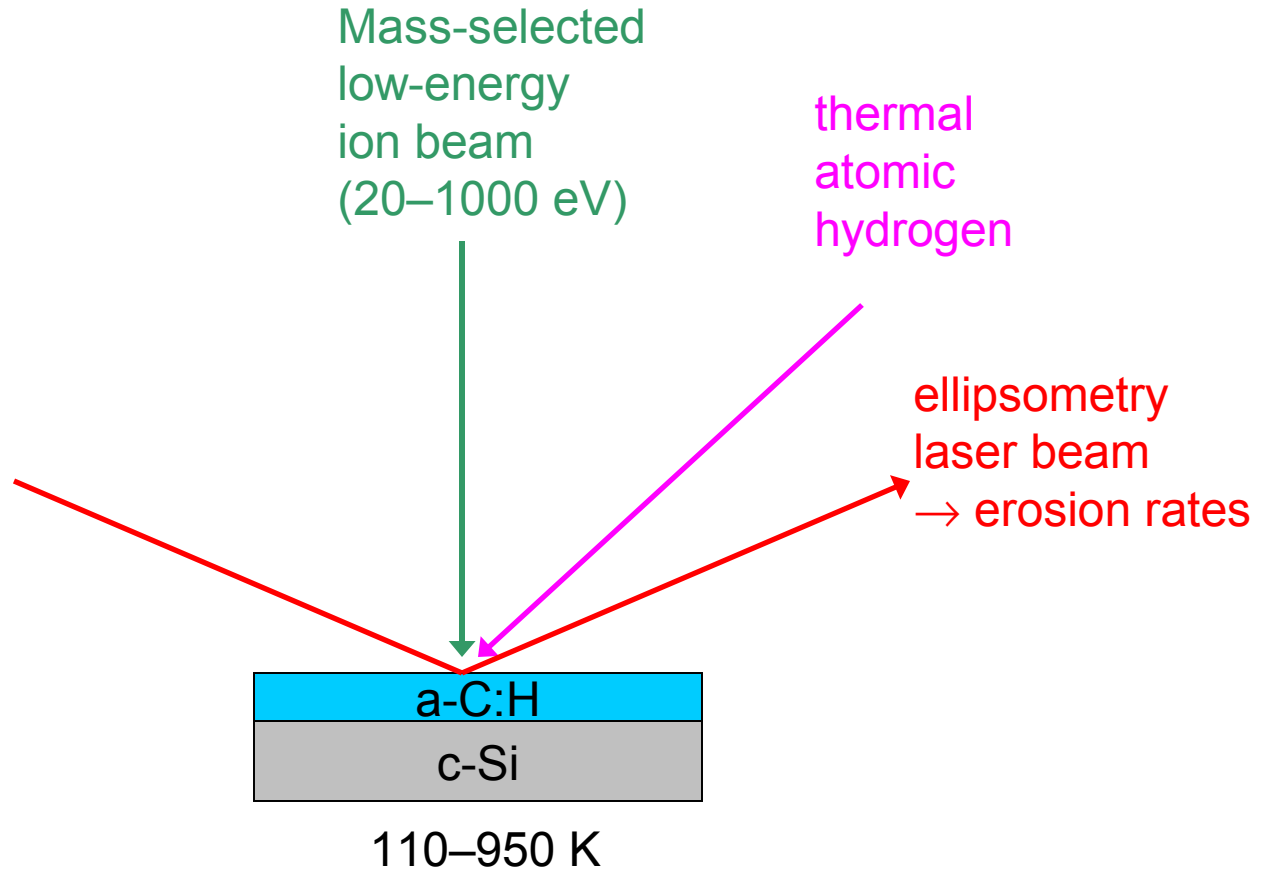
→ chemical sputtering

To improve mechanistic understanding:

2 separate beams: ions and thermal H^0

→ decouple damage creation and supply of reactive species

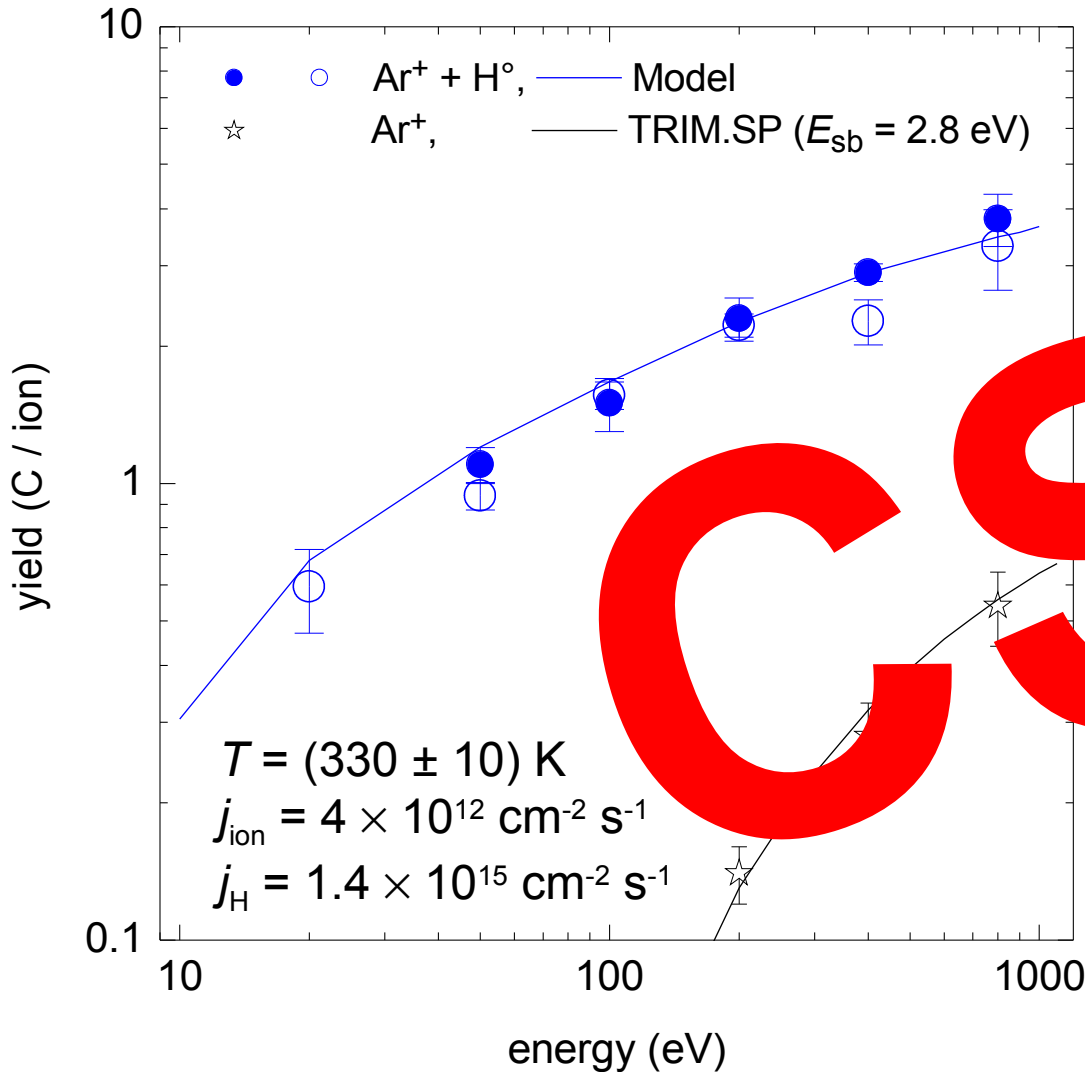
- Motivation
- Particle beam experiment MAJESTIX
- **Experimental data set / Phenomenology**
- **The mechanisms at work and their description in a rate equation model**
- Summary



W. Jacob, C. Hopf, A. von Keudell, M. Meier, T. Schwarz-Selinger,
Rev. Sci. Instrum. 74 (2003) 5123

The experimental data / Phenomenology

Ar⁺ + H⁰: Energy dependence



CS

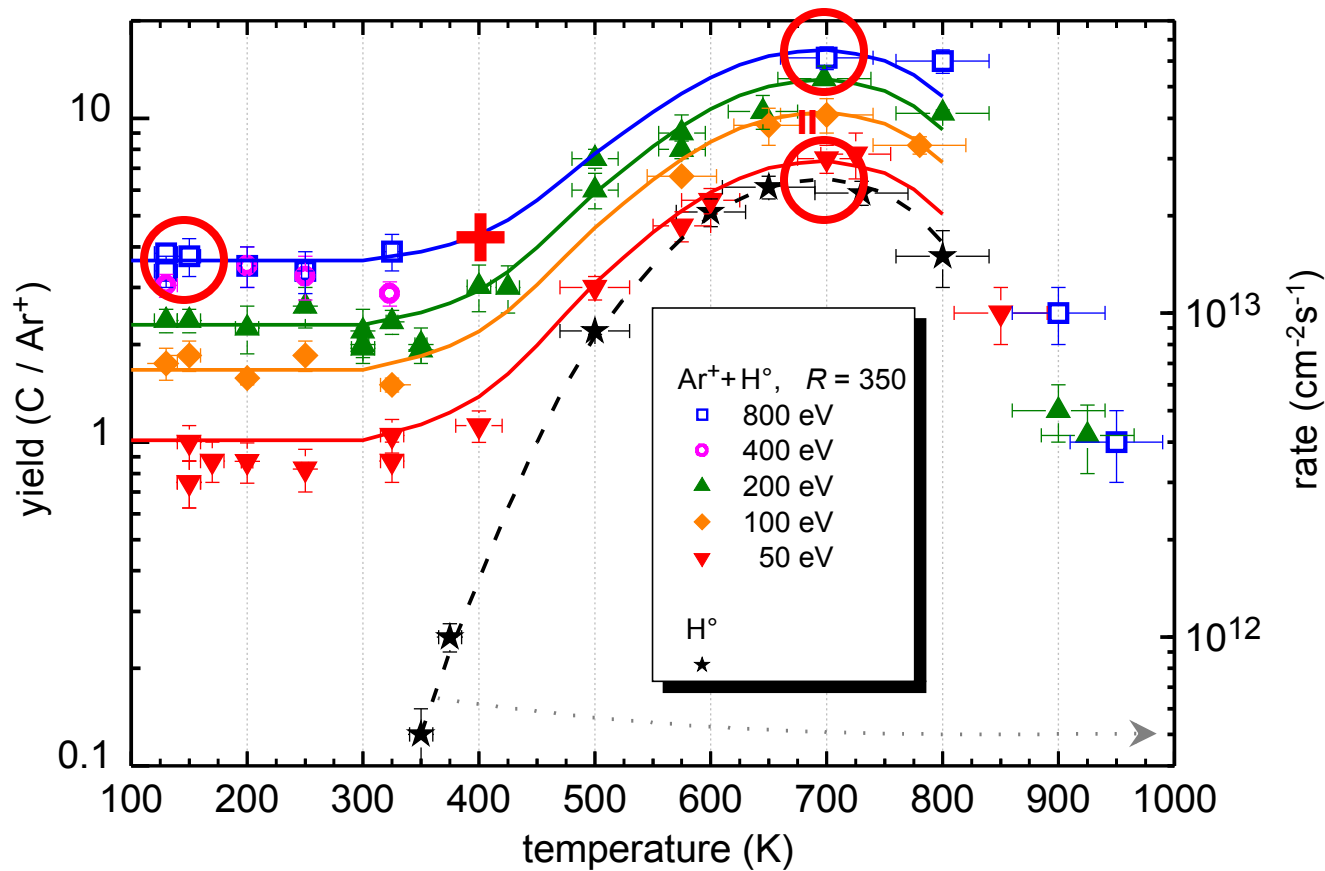
Clear enhancement of erosion compared to physical sputtering (PS) with Ar ions only.

Chemical sputtering (CS)

C. Hopf, A. von Keudell, and W. Jacob, Nucl. Fusion 42 (2002) L27

C. Hopf, A. von Keudell, and W. Jacob, J. Appl. Phys. 94 (2003) 2373

Temperature dependence



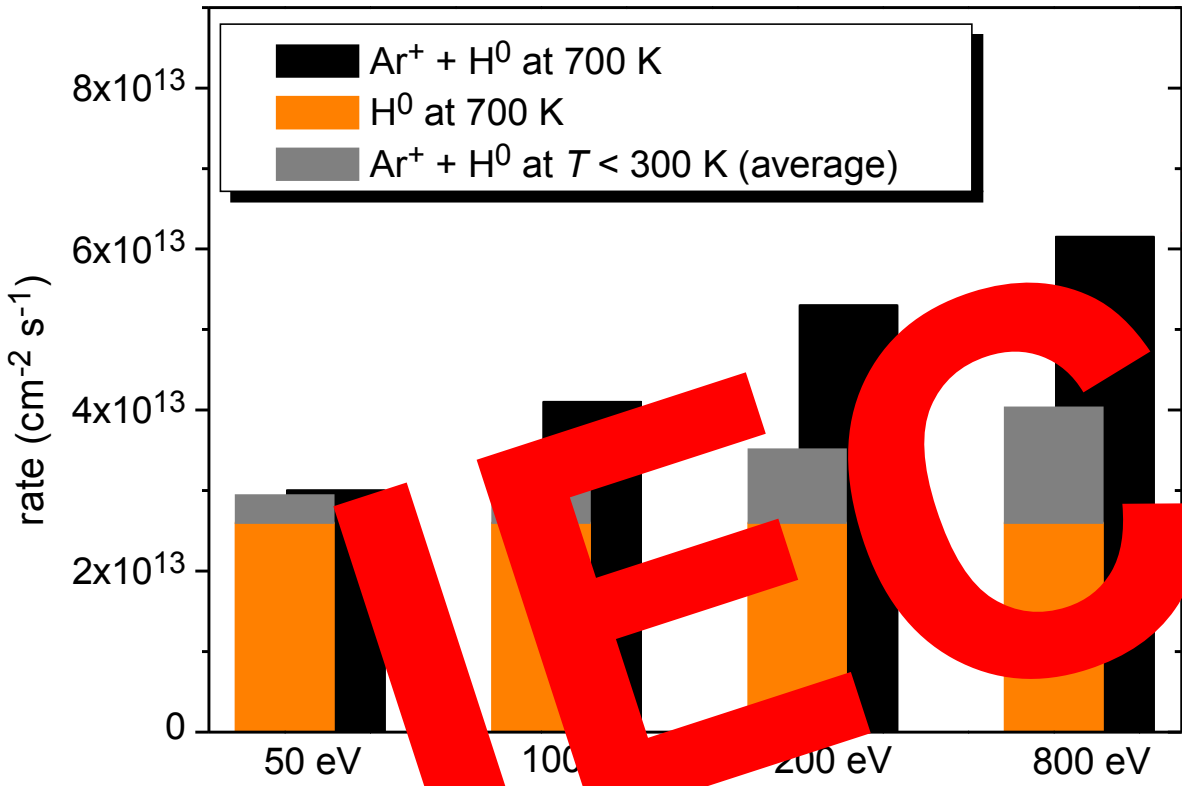
Thermal chemical erosion (CE) due to H° detectable from about 350 K

Ar^+ bombardment enhances erosion also at high temperatures

No temperature dependence at low T

M. Schlüter, C. Hopf, T. Schwarz-Selinger, W. Jacob, J. Nucl. Mater. 376 (2008) 33

Ion-enhanced chemical erosion



Measured rates @ 700 K

thermal chemical erosion rate
due to H^0

chemical sputtering rate due
to $Ar^+ + H^0$ at $T < 300$ K

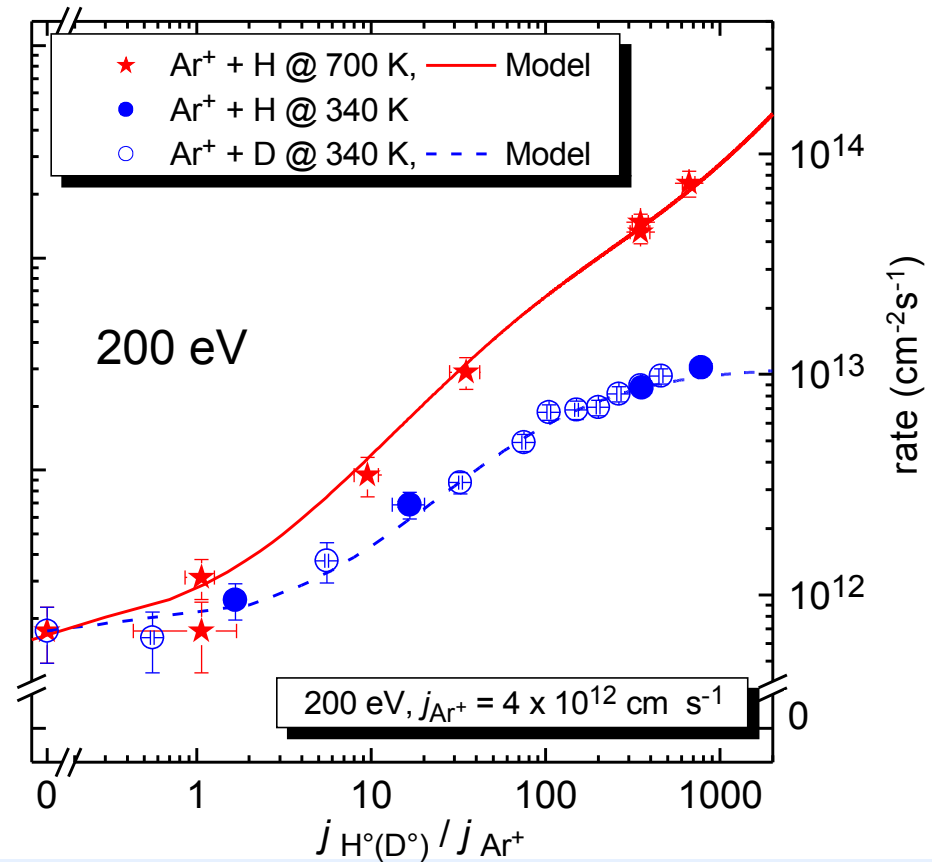
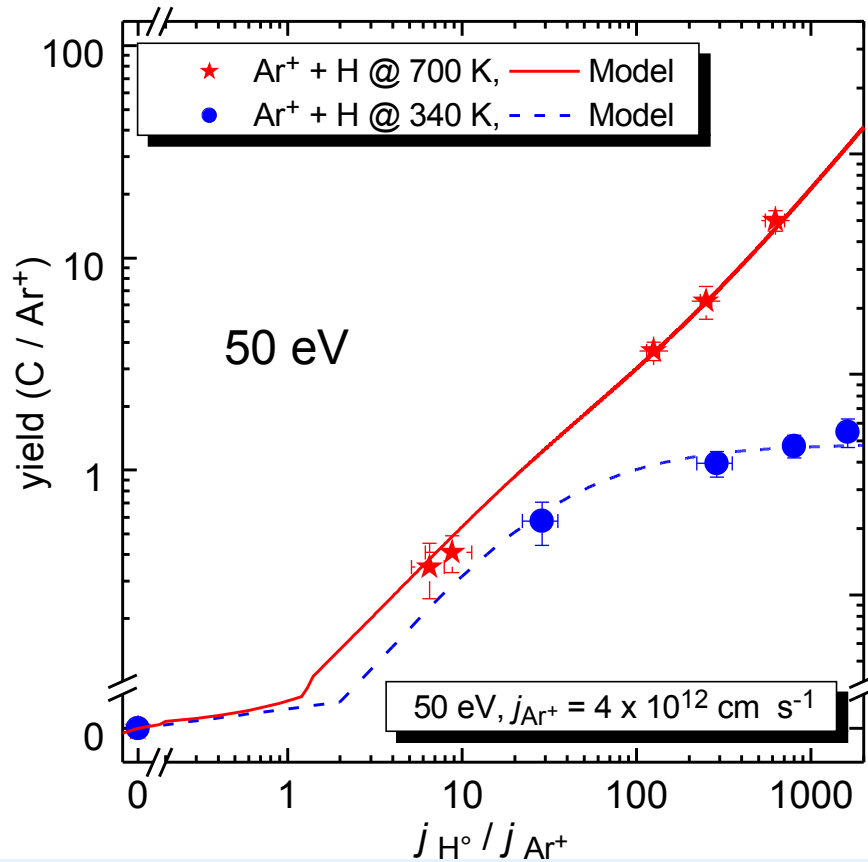


additional synergism:

Ion-Enhanced Chemical Erosion (IECE)

IECE

Flux dependence



340 K: Erosion yield / rate saturates at high $R = j_H / j_{ion}$.

700 K (maximum of chemical erosion): Erosion rate continues to increase with H flux.
 At high R erosion rate = $j_H \times Y_{therm}$

No isotope effect ($Y[Ar + H] = Y[Ar + D]$).

The mechanisms at work and their description with a rate equation model

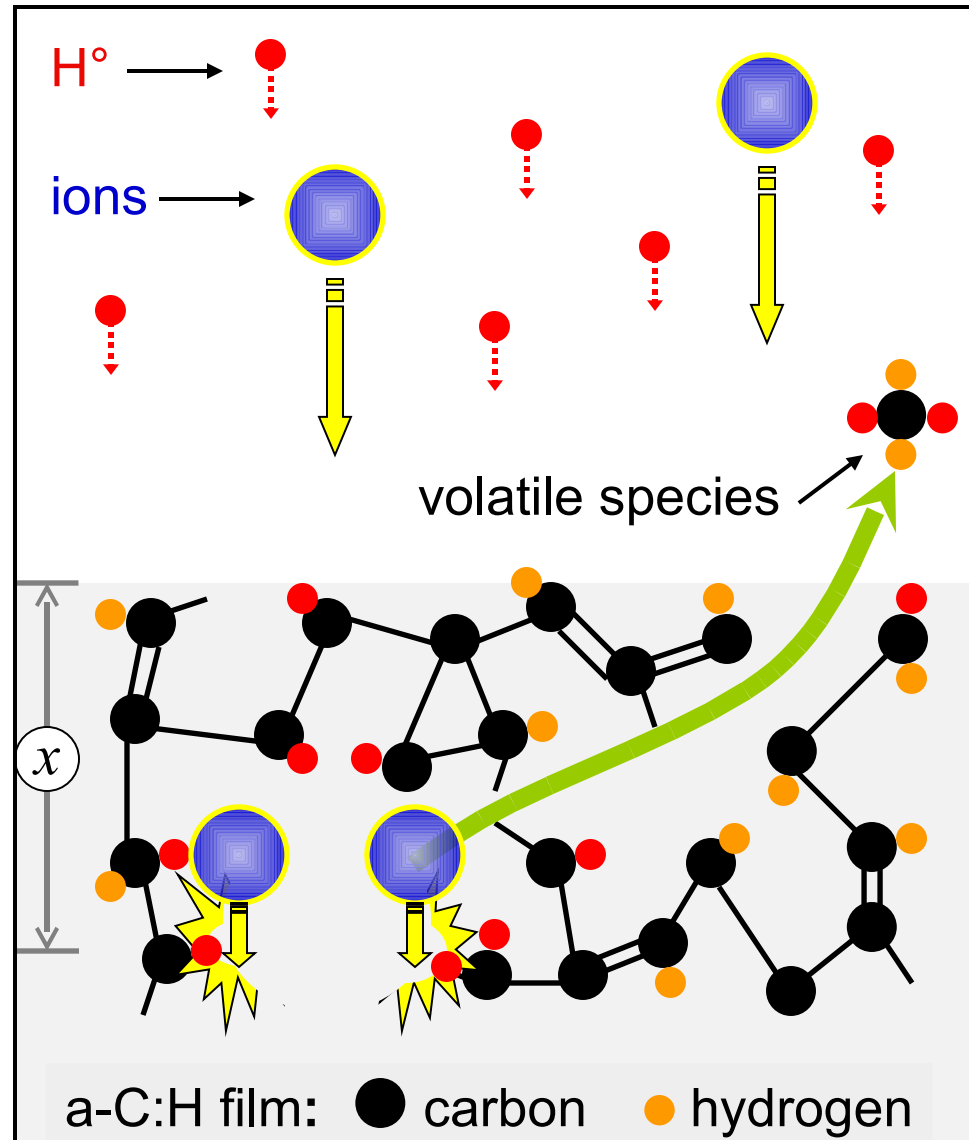
Basic mechanistic picture of chemical sputtering (CS)

Ions break C–C bonds.

H binds to these bonds and prevents their recombination.

Repeated bond breaking and H attachment incrementally “unhinges” a hydrocarbon molecule from the carbon network.

As soon as a last bond of a hydrocarbon molecule to the carbon network is broken, the molecule leaves the film surface.



Support from Molecular Dynamics Simulations

Simulation:

HCPaCas code (Kai Nordlund)

Brenner potential for C–C and C–H

Sample:

H/(H+C) = 0.38

930 Atoms in a 14 x 14 x 28 Å³ cell

periodic boundary conditions

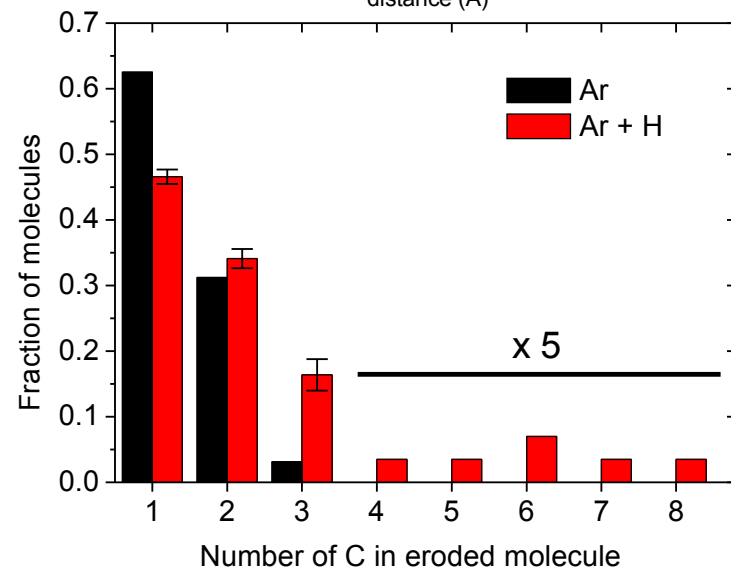
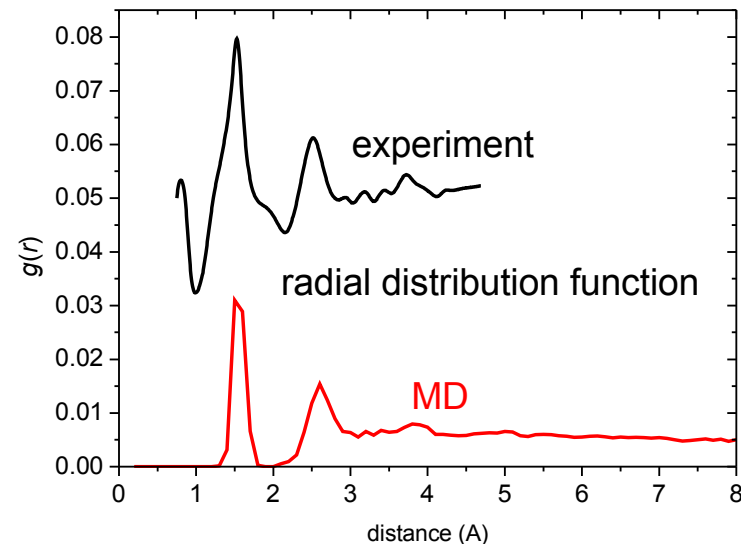
Bombardment simulations:

Ar ions of 150 eV at 45°

Sequence: 13 x (1 Ar + 50 H) + 1 Ar

Observations (HEPS = H enhanced phys. sputt.):

- Bond-breaking and passivation occur.
- Steric repulsion of neighbouring bonded H prevents recombination of broken bonds.
- Erosion product leaves after final bond to film is broken by ion impact. $\langle E \rangle \sim 1$ eV
- Yield $\sim 4 \times Y_{\text{phys}}$



Description of the energy dependence:

$$Y_{\text{CS}} = a \int y_{\text{bb}}(x, E) \exp(-x/\lambda) dx$$

$y_{\text{bb}}(x, E, (Z, A)) :$

Bond-breaking events per ion and unit depth interval calculated with TRIM.SP assuming C–C bond-breaking energy of 5 eV.

a : scaling factor

$\exp(-x/\lambda)$: restriction to near-surface layer, $\lambda = 0.4 \text{ nm}$

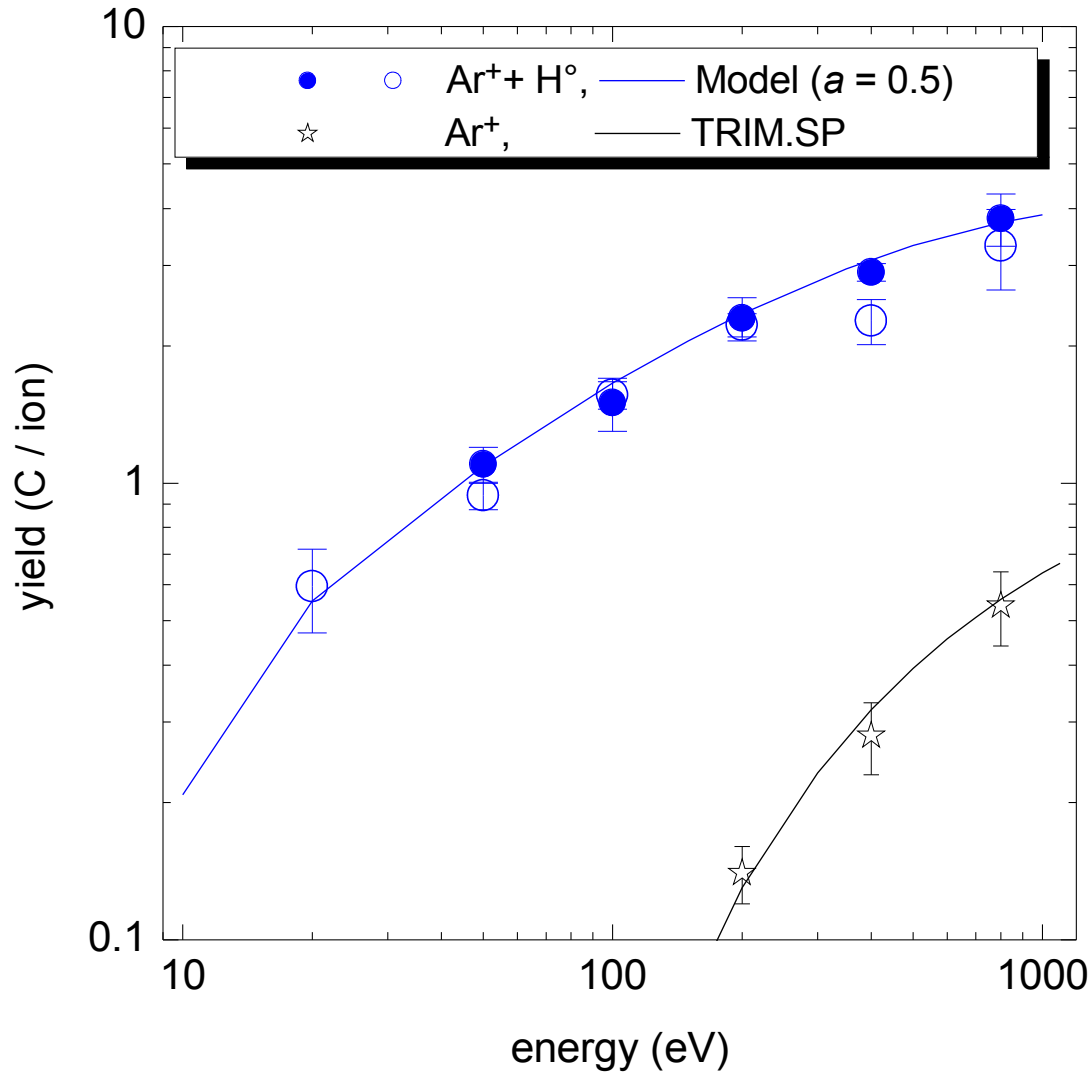
Ions break C–C bonds.

H binds to these bonds and prevents their recombination.

Repeated bond breaking and H attachment incrementally “unhinges” a hydrocarbon molecule from the film.

As soon as a last bond of a hydrocarbon molecule to the carbon network is broken, the molecule leaves the film surface.

Ar⁺ + H⁰: Energy dependence

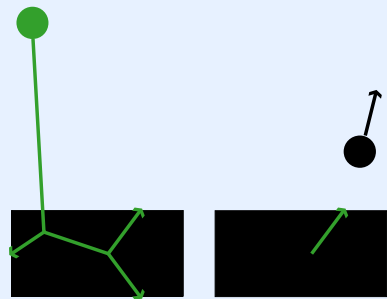


C. Hopf, A. von Keudell, and W. Jacob, Nucl. Fusion 42 (2002) L27

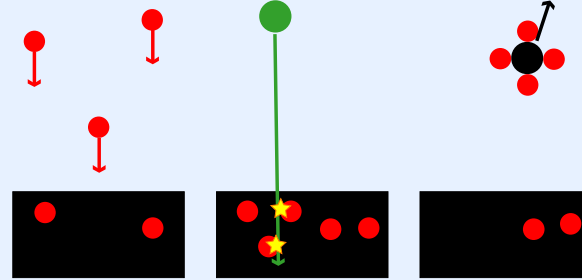
C. Hopf, A. von Keudell, and W. Jacob, J. Appl. Phys. 94 (2003) 2373

Rate equation model: Energy, flux, and temperature dependence

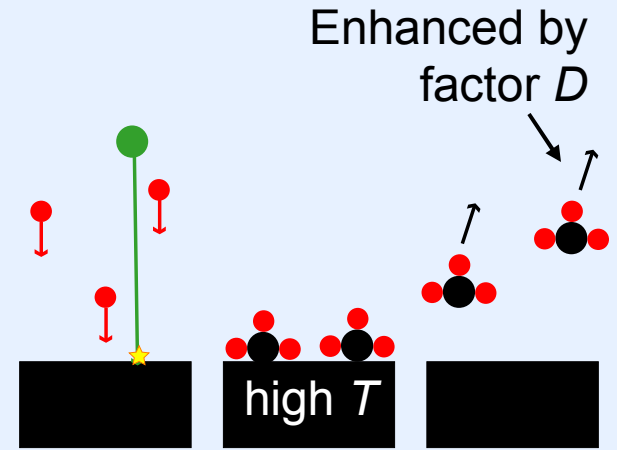
Erosion processes



Physical **S**puttering
(PS)



Chemical **S**puttering
(CS)



Chemical **E**rosion /
Ion-Enhanced **CE**
(CE / IECE)

Balance of surface coverages

process	rate	Θ_C	Θ_{CH}	Θ_r
(a) H incorporation	$j_{HP} j_{in}^H (1 - \Theta_{CH})$	→	←	
(b) creation of reactive sites	$j_{ion} Y_r (1 - \Theta_{CH} - B\Theta_r)$	→		
(c) ion-induced H depletion	$j_{ion} Y_{out}^H \Theta_{CH}$	←		
(d) CS	$j_{ion} Y_{CS} \Theta_{CH}$	←		
(e) IECE	$j_H Y_{therm} D \Theta_r$	←		

Energy-, Z- and A-dependent quantities:

Estimated using TRIM.SP: $CS \propto \int y_{bb}(x, E) \exp(-x/\lambda) dx$
Creation of reactive surface sites $\propto PS$

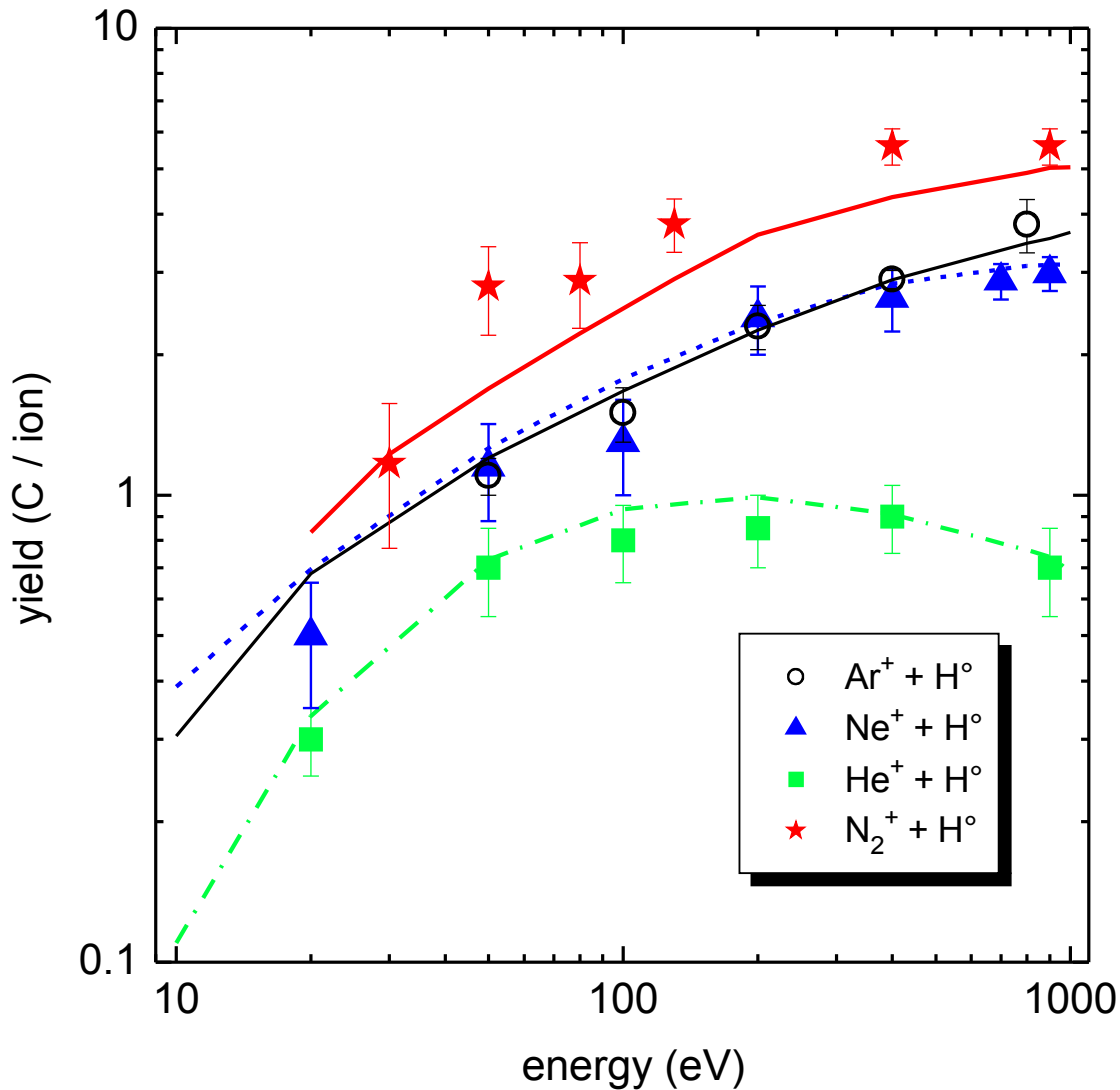
Thermal chemical erosion (CE) yield:

Fit to the experimental data points of CE (H^0 -only experiments) taken as input for the model.

Determination of the model's 5 free parameters:

Least-square fit to the experimental data points.

Model–Data comparison: Energy dependence

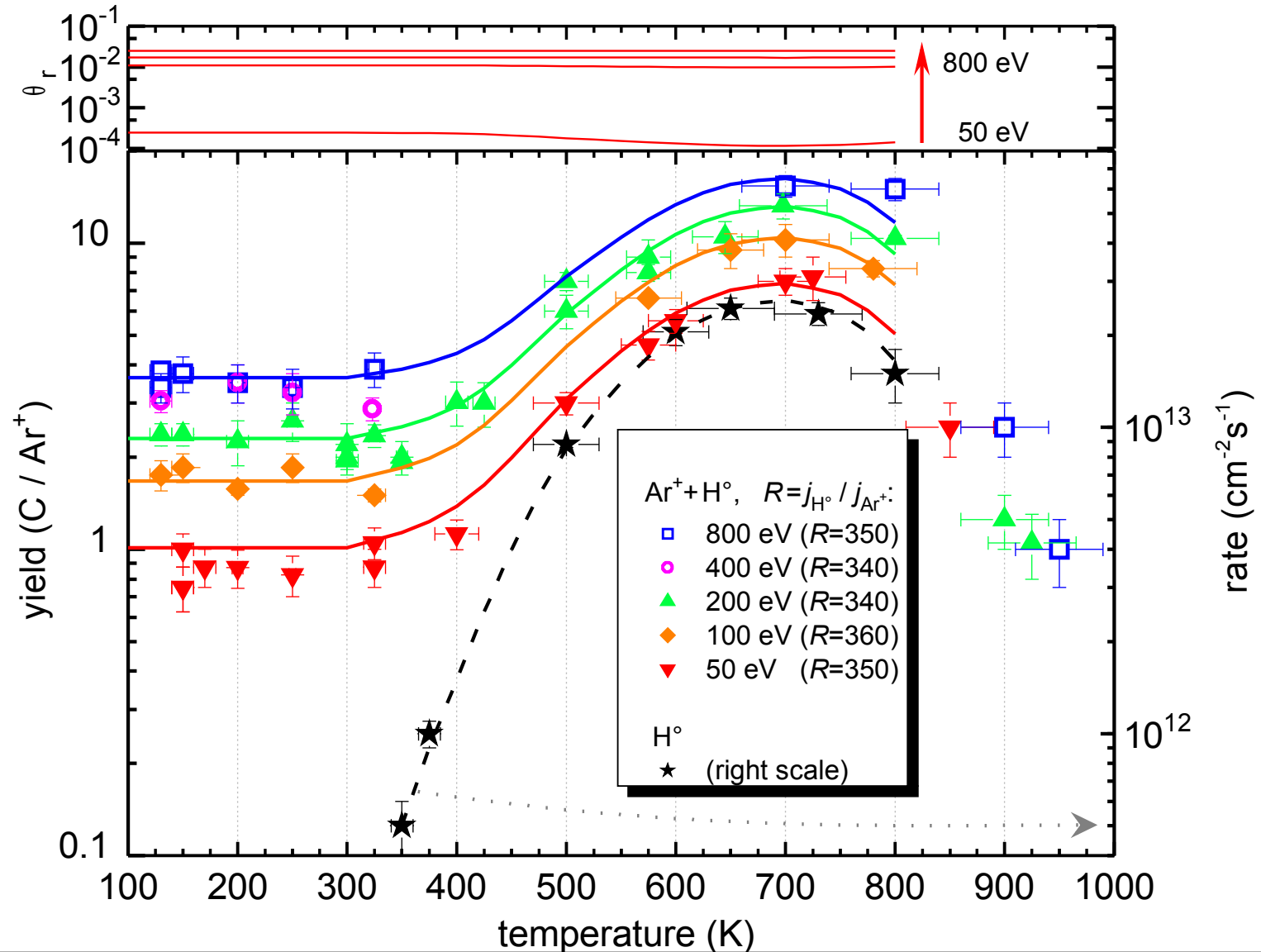


Model describes also the energy dependence of ion + H experiments with ions other than Ar^+ .

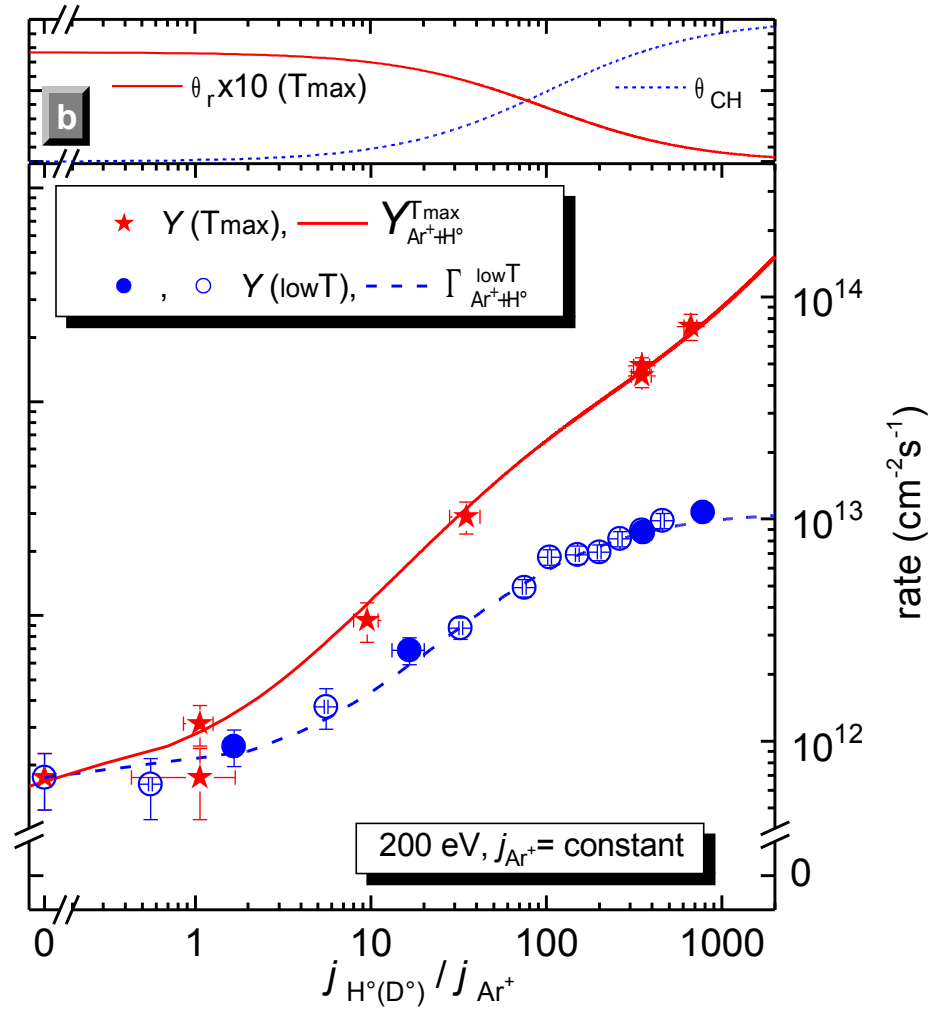
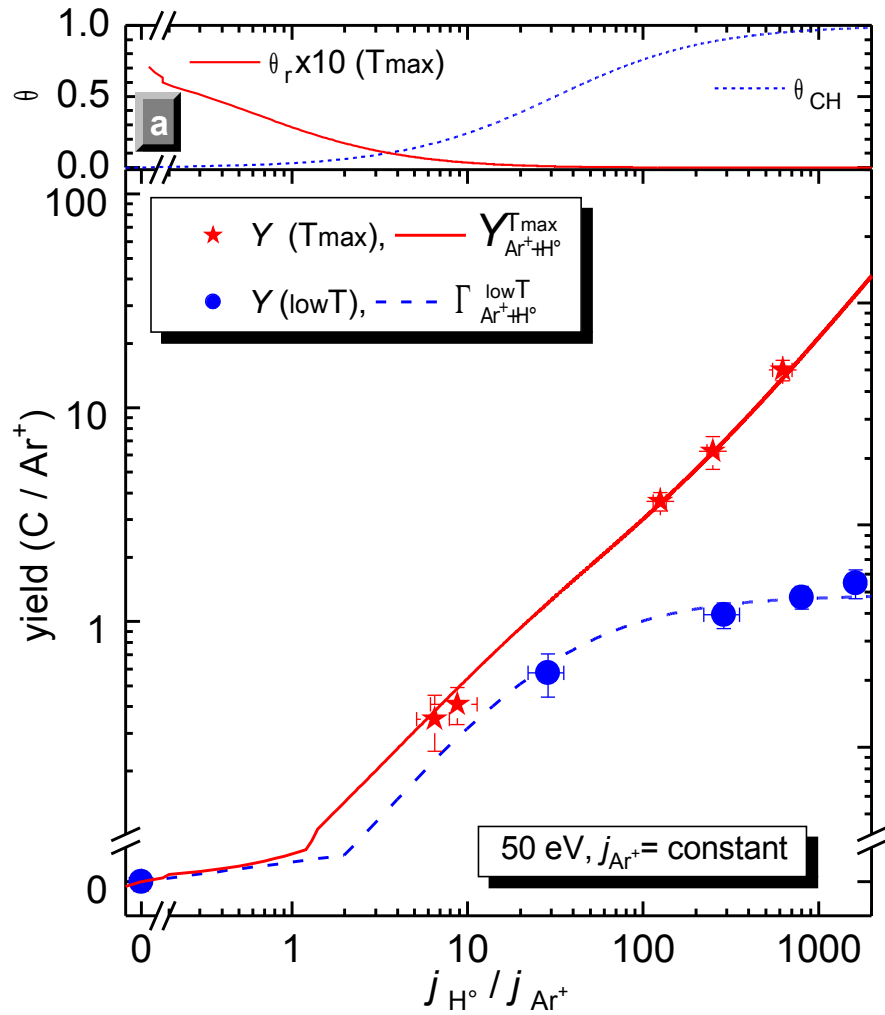
Exception: N_2^+

The N_2^+ 's own chemical sputtering adds to the ion-plus-H synergism

Model-Data comparison: Temperature dependence



Model-Data comparison: Flux dependence



We find two synergistic erosion mechanism for combined ion/H⁰ bombardment:

- Chemical sputtering at low T
- Enhancement of thermal chemical erosion at high T

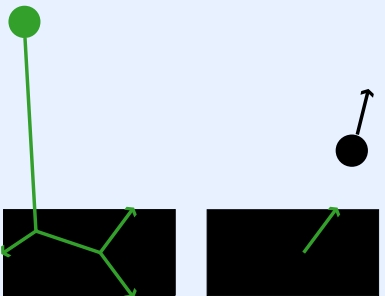
In both cases the effect of the ions is damage creation:

- CS: Yield \propto bond breaking in a near-surface layer
- IECE: Yield \propto physical sputtering yield

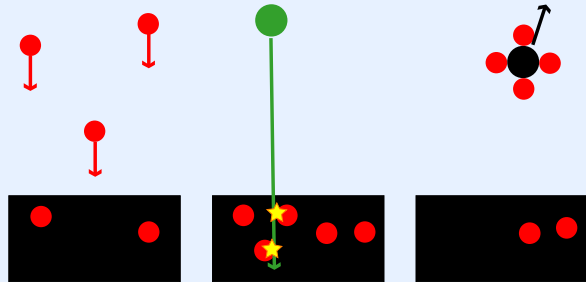
The mechanism of CS is repeated C–C bond breaking and attachment of H to the dangling bonds leading to incremental unhinging of C_xH_y molecules.

MD simulations basically support this picture.

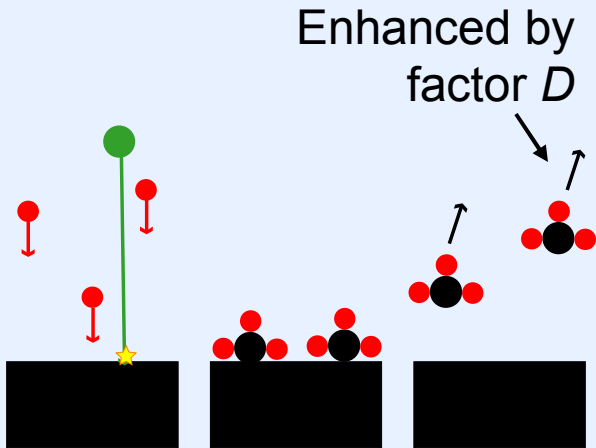
Erosion processes



Physical Sputtering (PS)



Chemical Sputtering (CS)



Chemical Erosion / Ion-Enhanced CE (CE / IECE)

Three coverages

- Θ_C : undisturbed carbon sites
- Θ_{CH} : C with "ready-to-react" H in the vicinity
- Θ_r : reactive sites (e. g. dangling bonds)

$$\Theta_C + \Theta_{CH} + \Theta_r = 1$$

Rate equation model: Energy, flux, and temperature dependence

Three coverages

- Θ_C : undisturbed carbon sites
- Θ_{CH} : C with “ready-to-react” H in the vicinity
- Θ_r : reactive sites (e. g. dangling bonds)

$$\Theta_C + \Theta_{CH} + \Theta_r = 1$$

Erosion rate

$$\Gamma = \Gamma_{PS} + \Gamma_{CS} + \Gamma_{CE} + \Gamma_{IECE}$$

$$\Gamma = j_{ion} Y_{PS} + j_{ion} Y_{CS} \Theta_{CH} + j_H Y_{therm} (1 + D \Theta_r)$$

Balance of surface coverages

process	rate	Θ_C	Θ_{CH}	Θ_r
(a) H incorporation	$j_H P_{in}^H (1 - \Theta_{CH})$	→	←	
(b) creation of reactive sites	$j_{ion} Y_r (1 - \Theta_{CH} - B \Theta_r)$	→		
(c) ion-induced H depletion	$j_{ion} Y_{out}^H \Theta_{CH}$	←		
(d) CS	$j_{ion} Y_{CS} \Theta_{CH}$	←		
(e) IECE	$j_H Y_{therm} D \Theta_r$	←		

Balance of surface coverages

process	rate	Θ_C	Θ_{CH}	Θ_r
(a) H incorporation	$j_{HP} j_{in}^H (1 - \Theta_{CH})$	→	←	
(b) creation of reactive sites	$j_{ion} Y_r (1 - \Theta_{CH} - B\Theta_r)$	→		→
(c) ion-induced H depletion	$j_{ion} Y_{out}^H \Theta_{CH}$	←		
(d) CS	$j_{ion} Y_{CS} \Theta_{CH}$	←		
(e) IECE	$j_H Y_{therm} D\Theta_r$	←		←

Three energy-dependent quantities

$Y_{PS}(E)$: TRIM.SP with $E_{sb} = 2.8 \text{ eV}$

$$Y_{CS}(E) = a_{CS} \int y_{bb}^{C-C}(x, E) \exp(-x/\lambda) dx \quad \text{with } E_{bb}^{C-C} = 5 \text{ eV}$$

$$Y_{out}^H(E) = a_H \int y_{bb}^{C-H}(x, E) \exp(-x/\lambda) dx \quad \text{with } E_{bb}^{C-H} = 2.5 \text{ eV}$$

$$Y_r(E) = a_r Y_{PS}(E)$$

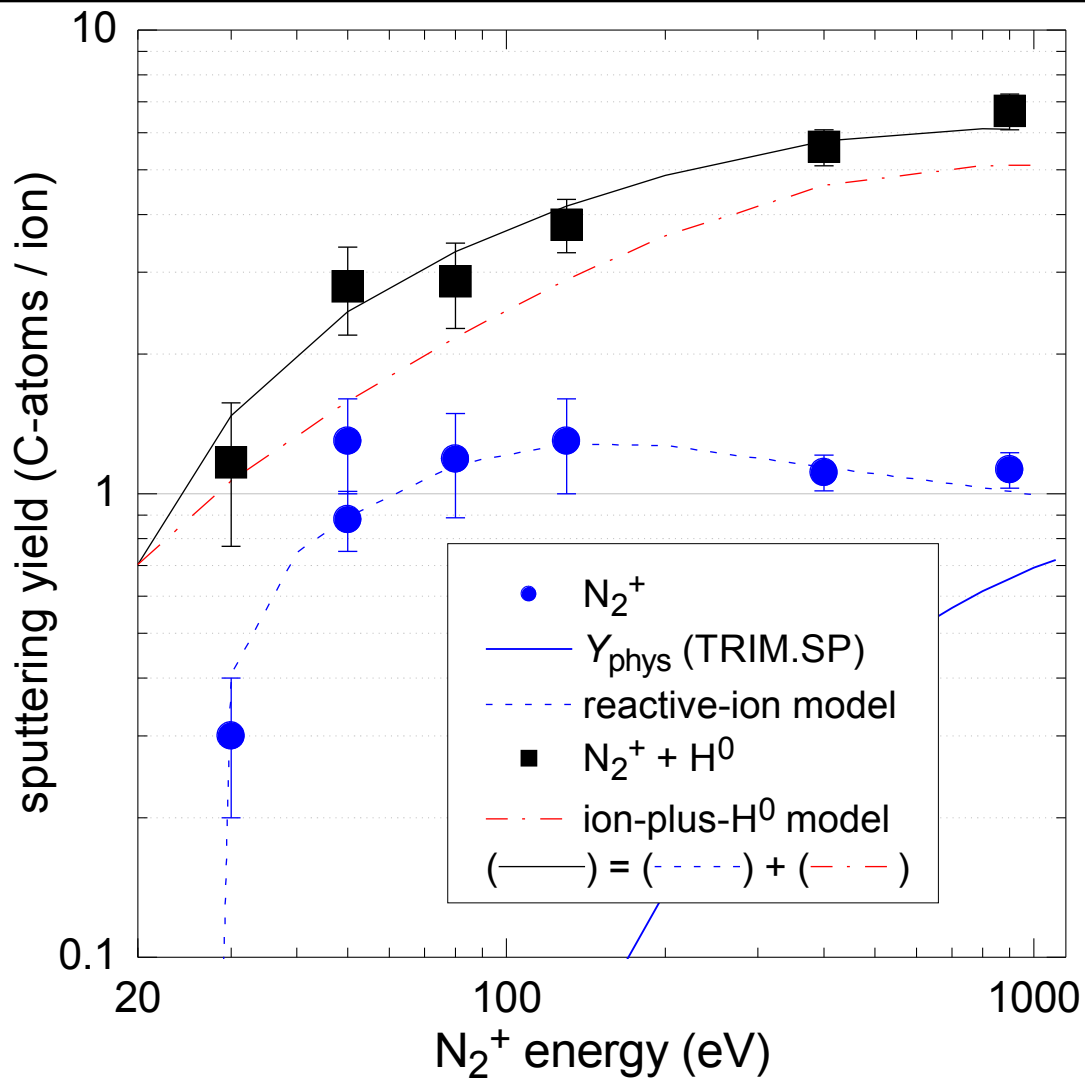
Temperature dependence:

Take a fit to the measured thermal chemical erosion yield as input for the model.

Fit of the models 5 free parameters to the data:

Parameter	Wert	Bemerkung
a_{cs}	0,60	Vorfaktor bei Y_{cs}^E in Gl. 4.2
a_H	31,4	Vorfaktor bei $Y_{H^{out/in}}^E$ in Gl. 4.3
a_r	6207	Vorfaktor bei Y_r^E in Gl. 4.10
$D_{H^{\bullet}}$	37,0	Proportionalitätsfaktor bei IECE in Gl. 4.5
$p_{H^{\bullet}in}$	0,57	57 % des einkommenden Wasserstoffs werden eingebaut (Gl. 4.8)
B	13	für die Rekombination von benachbarten reaktiven Plätzen (Θ_r)
λ	0,4 nm	Abfalllänge für das Eindringen von H^{\bullet}

Other examples of chemical sputtering of a-C:H: N_2^+ ions

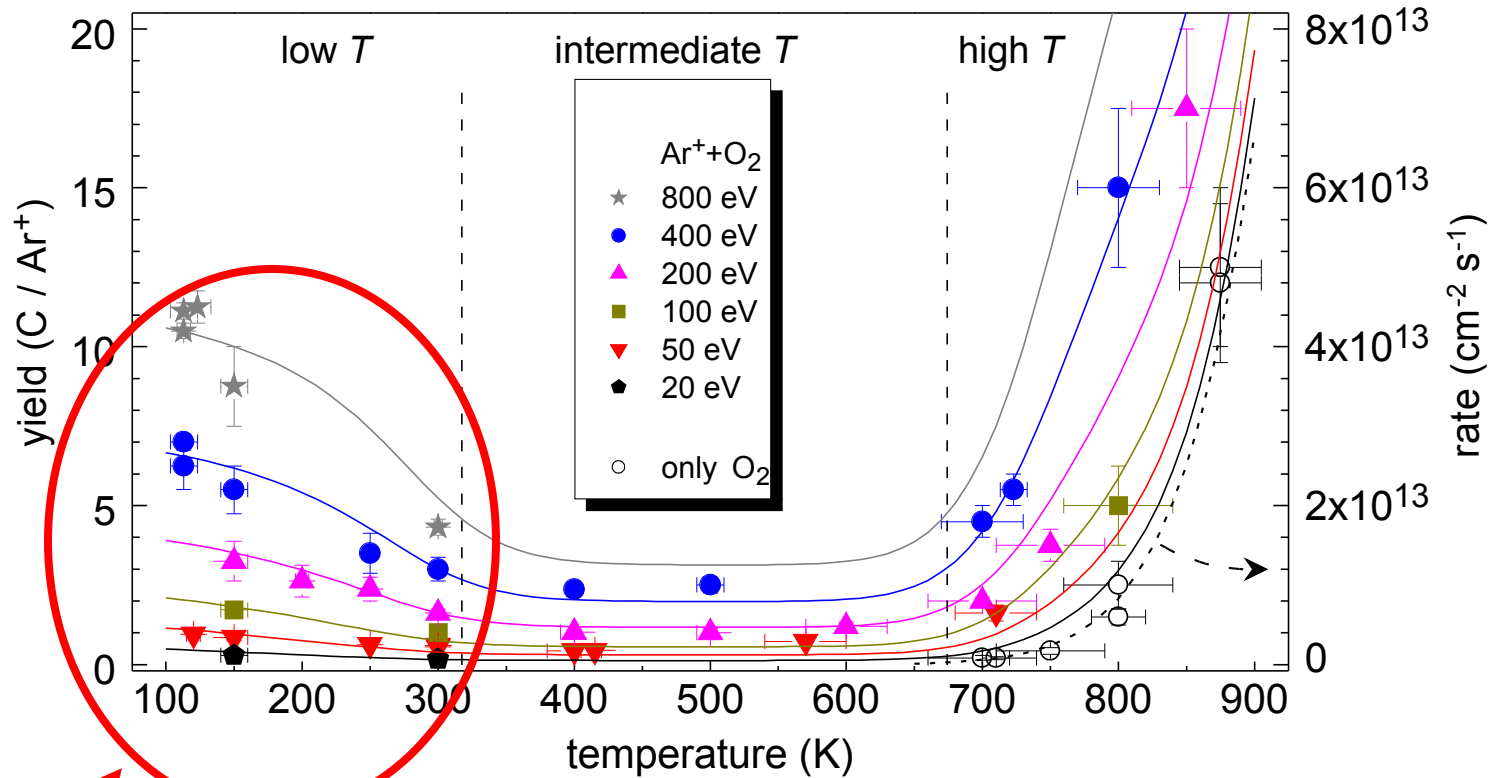


N_2^+ :
Like hydrogen ions, nitrogen ions cause chemical sputtering.

$N_2^+ + H_0$:
CS rate by N_2^+ adds to the CS rate of (inert N_2^+ -type) ions + H^0

M. Schlüter, C. Hopf, W. Jacob, New. J. Phys. 10 (2008) 053037

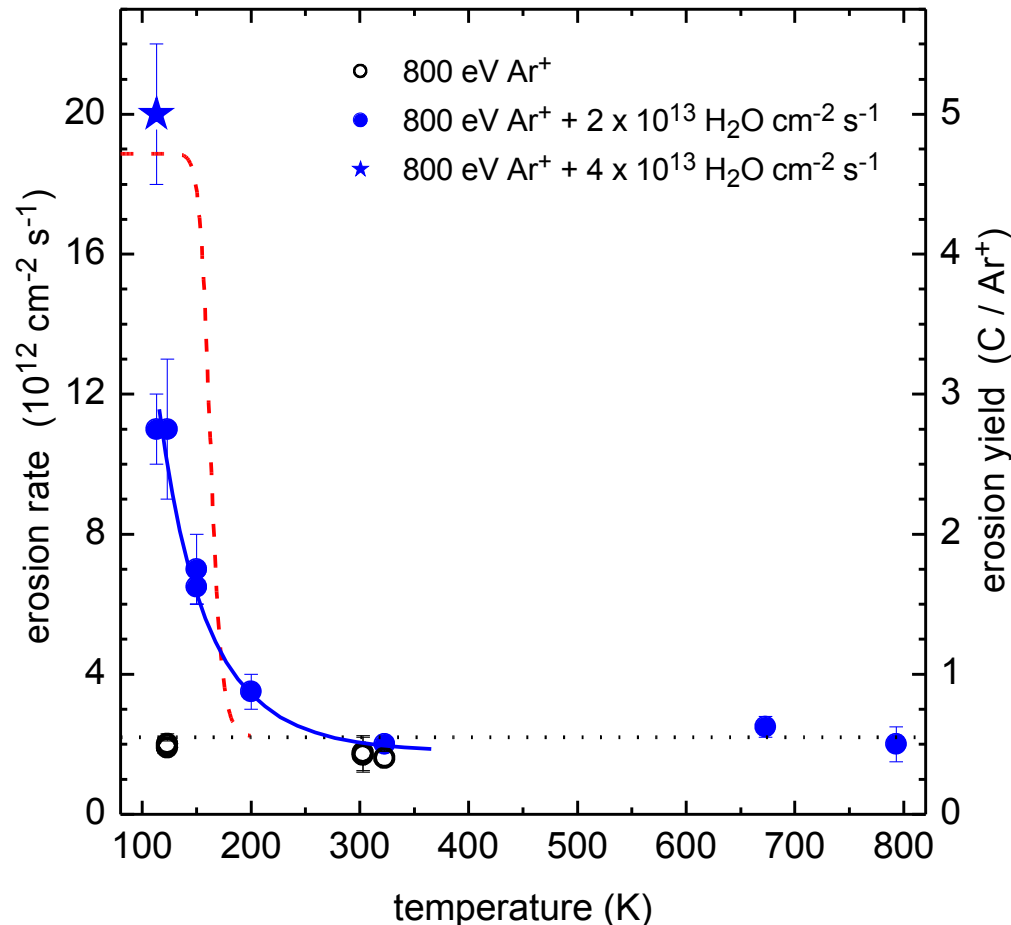
Other examples of chemical sputtering of a-C:H: thermal O₂



Enhanced erosion at low temperature:
 Ion-induced reaction b/w weakly adsorbed oxygen and the film
 (Adsorbed layer chemical sputtering [ALACS])

C. Hopf, M. Schlüter, T. Schwarz-Selinger, U. von Toussaint, W. Jacob,
 New. J. Phys. 10 (2008) 093022

Other examples of chemical sputtering of a-C:H: Water



Ion bombardment induces chemical reactions between adsorbed water molecules and the film.

Without ion bombardment continued growth of an ice layer is observed.

C. Hopf, M. Schlüter, W. Jacob, J. Phys.: Conf. Series 100 (2008) 062012

A definition of chemical sputtering:

Chemical sputtering is an erosion process in which the impact of energetic species induces chemical reactions that lead to the formation of volatile erosion products.

Different possible mechanisms, such as:

(9) Bonds are broken and incident species react. (CS)

(10) Ions induce reactions between adsorbed species and the surface atoms.
(ALACS)

(11) Damage created at the surface enhances the reactivity of the surface for thermal chemical erosion. (IECE)

Chemical sputtering occurs whenever the reactive species (either energetic itself or impinging simultaneously with other energetic species) can form volatile reaction products with the material to eroded.

