



2028-12

Joint ICTP/IAEA Workshop on Atomic and Molecular Data for Fusion

20 - 30 April 2009

Plasma-Wall Interaction in Magentic Fusion Erosion Mechanisms (Erosion of Carbon by Hydrogen)

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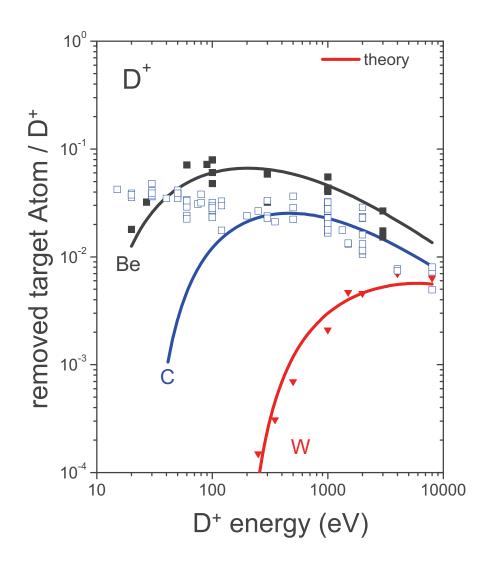
Thomas Schwarz-Selinger

erosion mechanisms (erosion of carbon by hydrogen)

- chemical erosion
- physical sputtering
- chemical sputtering

erosion by hydrogen impact at room temperature





- Advantage for high-Z materials
- Strong deviation for Carbon based materials
 - ⇒ what is different?
 - ⇒ chemical reactions betweenD and C formingvolatile hydrocarbons

research groups (experimental): erosion of carbon by hydrogen



> Roth:

- IPP, Garching-Germany

> Jacob:

- IPP, Garching-Germany

> Küppers:

- Experimentalphysik III, Universität Bayreuth, Bayreuth-Germany
- IPP, Garching-Germany

> Vietzke:

- Institut für Chemie, KFA Jülich GmbH, Jülich-Germany

> Haasz/Davis:

- Fusion research group, university of Toronto, Ontario-Canada
- Institute for Aerospace Studies and Centre for Nuclear Engineering, Ontario-Canada

nomenclature



- <u>Chemical erosion</u> is a selective removal of surface atoms by *chemical reactions*, forming volatile reactants that can desorb.
- <u>Physical sputtering</u> is the *kinetic ejection of surface atoms* by incident energetic ions or atoms *due to collision processes*.
 (playing billiards with surface atoms).
- <u>Chemical Sputtering</u> is 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 desorbs in the gas phase.



CHEMICAL EROSION IN FUSION DEVICES:

FORMATION OF HYDROCARBONS:

H C $CH_4 (+C_xH_y)$

FORMATION OF CARBON OXIDES:

O C $CO + CO_2$

REACTIONS WITH SOME METALS:

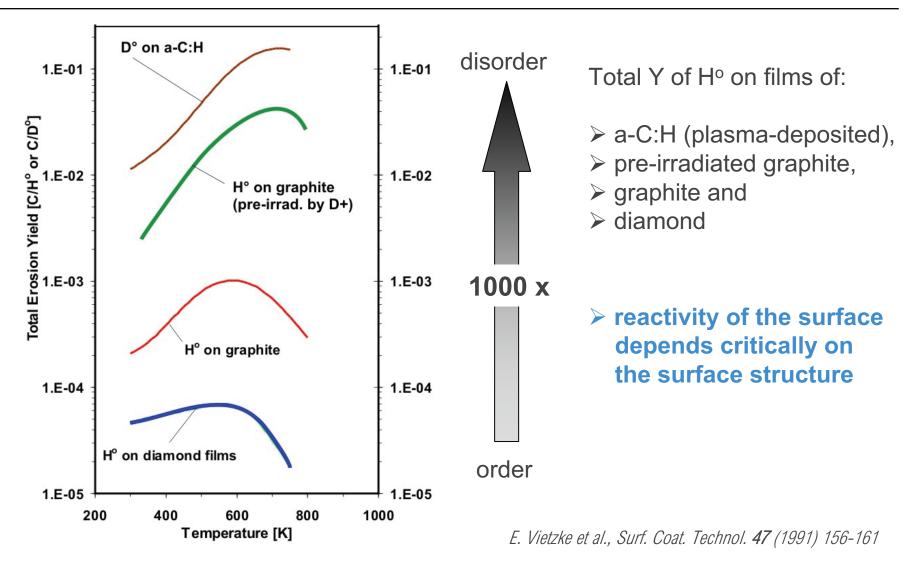
O Me Me (O) (W above 1000 °C)

H Me (O) Me (OH) H Me (OH) Me + H_2 O

Thomas Schwarz-Selinger, IAEA Workshop on Atomic and Molecular Data for Fusion Energy Research, August 28 - September 8, 2006, Abdus Salam International Centre for Theoretical Physics, Trieste

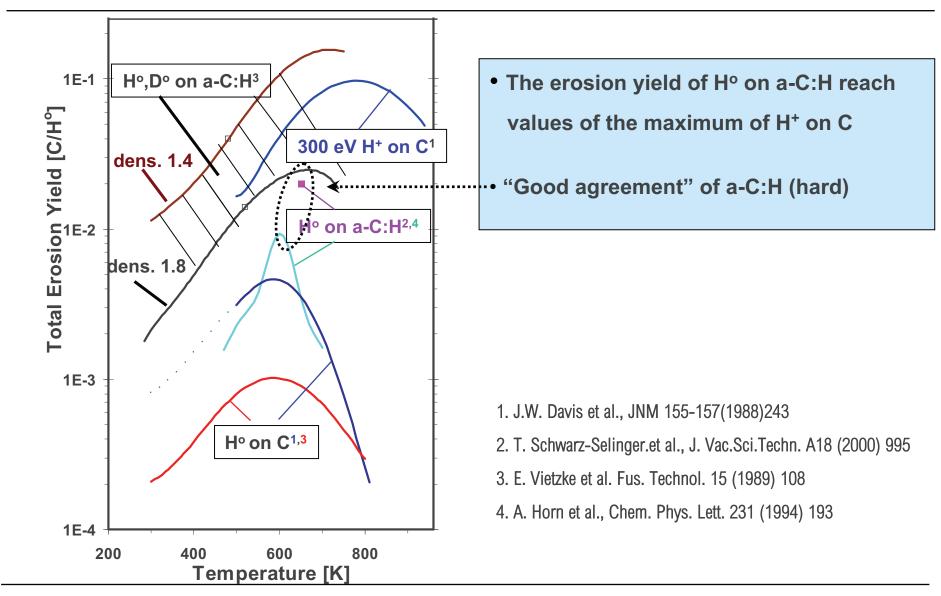
chemical erosion of carbon: structure dependence





chemical erosion of carbon: structure dependence





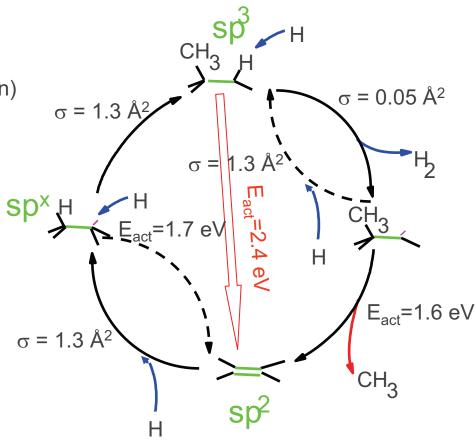
chemical erosion: microscopic model



Hydration and erosion circle:

Horn et al., Chem. Phys. Lett. 231, 193 (1994) Zecho et al.J. Phys. Chem. B 105 (2001).

- 1) chemisorption of H on sp² site
- 2) chemisorption of H on sp^x site (hydration)
- 3) abstraction of H to form H₂
- 4 a) thermal release of CH₃ radicals from activated sites above 400 K
- 4 b) chemisorption of H on sp^x site
- 5) relaxation back to sp² above 750 K
- 6) direct thermal decomposition to sp^2 above 900 K with E_{act} =2.4 eV



chemical erosion: microscopic model



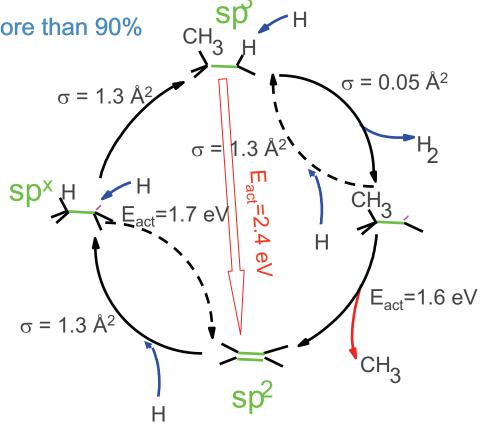
hydration and erosion circle:

Horn et al., Chem. Phys. Lett. 231, 193 (1994) Zecho et al.J. Phys. Chem. B 105 (2001).

 hydration at room temperature of more than 90% of all possible adsorption sites

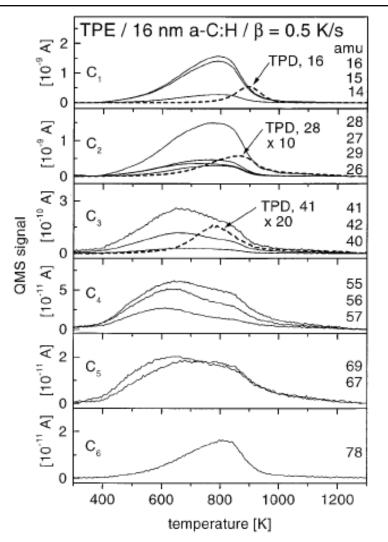
- erosion maximum
- flux dependence of the erosion maximum

600 K at 10¹⁷ m⁻²s⁻¹ 750 K at 10²⁰ m⁻²s⁻¹ ??? K at 10²⁴ m⁻²s⁻¹ (ITER)

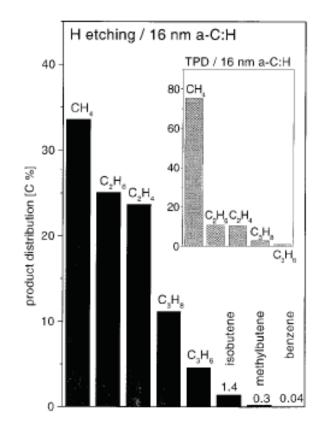


chemical erosion: product distribution





Formation of volatile C_xH_y :
Thermal <u>decomposition</u> and <u>erosion</u>
with H^o of dense a-C:H film

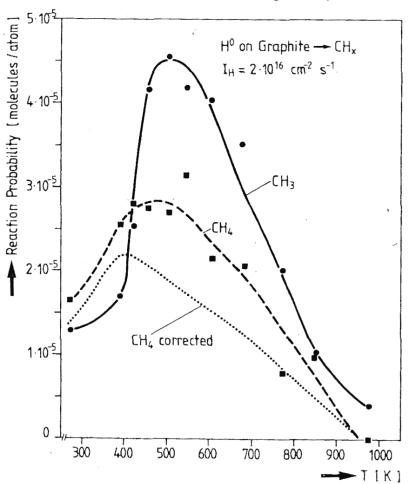


T. Zecho, B. D. Brandner, J. Biener, J. Küppers; J. Phys. Chem. B 105 (2001) 6194-6201

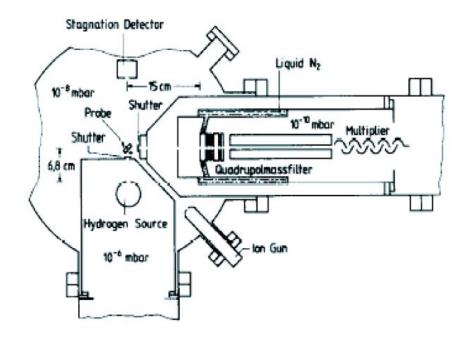
chemical erosion: direct identification of the precursor



At T=500K \rightarrow ratio CH₃/CH₄ ~ 2



dedicated experiment to detect reactive products:



E. Vietzke, K. Flaskamp, V. Philipps.; J. Nucl. Mater. 128-129 (1984) 545-550

chemical erosion: present status



erosion of dense a-C:H

- ▶Precursor for chemical erosion is a CH₃ group (C₂H_x) adjacent to a dangling bond site (both are produced by interaction with atomic hydrogen)
- ➤ cross section for hydrogenation (1.3 Ų) and abstraction (0.05 Ų) and threshold energies for relaxation (2.4 eV / 1.7 eV) are known (within a factor of 2?)
- > nearly all eroded material is transferred into none-reactive volatile products
- ➤ shows no isotope effect (generally assumed)

erosion of soft a-C:H

➤ thermal decomposition above 600 K and redeposition of up to 50% of the material

chemical erosion: present status



open questions for ITER

- ➤ high flux limit of the model
- influence of material mix?
- ➤ impact of vibrationally excited molecules on erosion?

chemical erosion



- Chemical erosion originates from the formation and release of volatile molecules in the interaction of incident plasma particles and target atoms.
- In fusion application the formation of hydrocarbons in the interaction of hydrogen atoms with carbon surfaces is the dominant example of chemical erosion.
- As chemical reactions are involved, chemical erosion shows a strong temperature dependence in contrast to physical sputtering.
- Chemical erosion can occur with low-energy ions or thermal atoms and does not require a threshold energy.

nomenclature



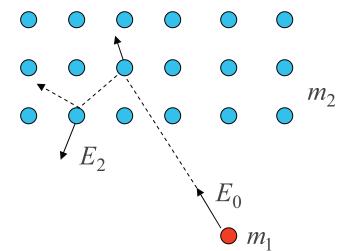
- <u>Chemical erosion</u> is a selective removal of surface atoms by chemical reactions, forming volatile reactants that can desorb.
- Physical sputtering is the kinetic ejection of surface atoms by incident energetic ions or atoms due to collision processes.
 (playing billiards with surface atoms).
- <u>Chemical Sputtering</u> is 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 desorbs in the gas phase.







sputter yield
$$Y = \frac{\text{average No of sputtered particles}}{\text{incident ion}}$$



energy transfer in central collision: $\gamma = 4 \frac{m_1 m_2}{(m_1 + m_2)^2}$

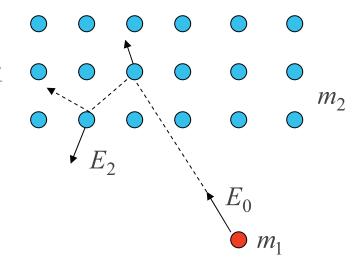
 $m_1 < m_2$, after first collision: $E_1 = E_0(1-\gamma)$

transferred energy: $E_2 = \gamma \cdot E_0 (1 - \gamma)$

threshold energy: $E_{\text{th}} = \frac{E_{\text{s}}}{\gamma(1-\gamma)}$ (E_{s} : surface binding energy) 3.5 eV < E_{s} < 9 eV



sputter yield
$$Y = \frac{\text{average No of sputtered particles}}{\text{incident ion}}$$

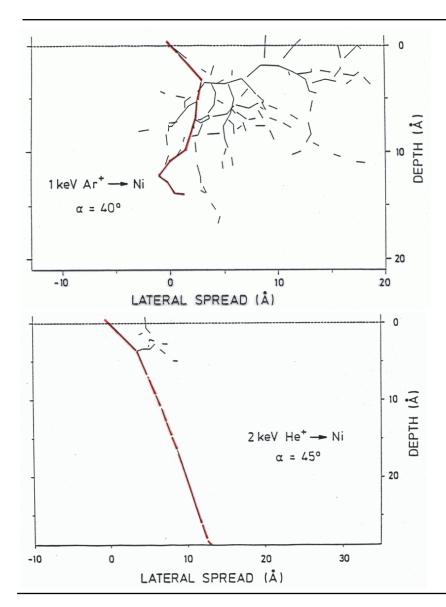


 $m_1 = m_2$ (extended collison cascade): $E_{th} = 4E_s$ (self sputtering), $3.5 \, \text{eV} < E_s < 9 \, \text{eV}$

self sputtering: if Y > 1: unlimited increase of impurity content

collision cascade





TRIM.Sp Monte-Carlo Code

heavy ions:

- large collision cascade
- isotropic velocity distribution
- yield proportional to energy deposited in first two layers

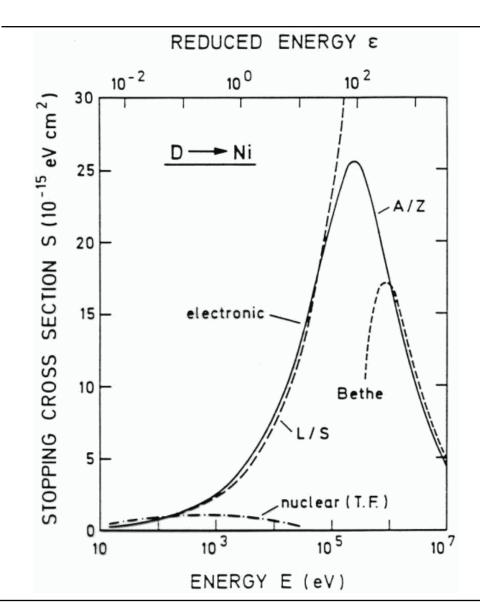
light ions:

- few collisions
- energy transfer in single collision

•
$$T = E_0 \frac{M_1 M_2}{(M_1 + M_2)^2} \cos^2 \delta$$

stopping power





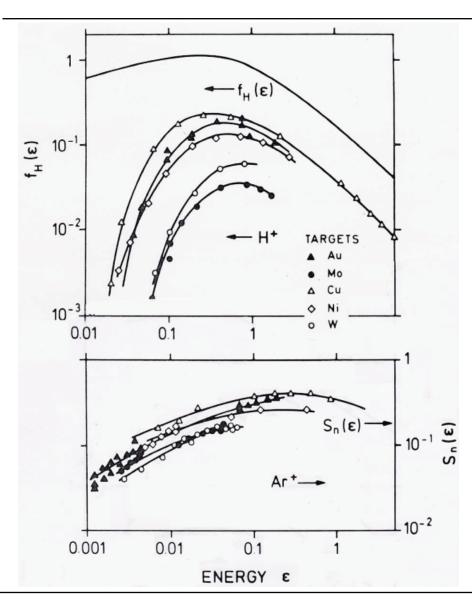
- projectiles and recoil atoms loose energy in elastic collisions (nuclear stopping) and collisions with electrons (inelastic stopping)
- the stopping cross section is a universal function if plotted versus the reduced energy ε

•
$$\epsilon = E_0 \frac{M_2}{M_1 + M_2} \frac{a}{Z_1 Z_2 e^2} = \frac{E_0}{E_{TF}}$$

•
$$S_n(\epsilon) = \frac{0.5 ln(1 + 1.2288\epsilon)}{\epsilon + 0.1728\sqrt{\epsilon} + 0.008\epsilon^{0.1504}}$$

theory for sputtering in isotropic collision cascades





Ansatz:

(P. Sigmund (1969))

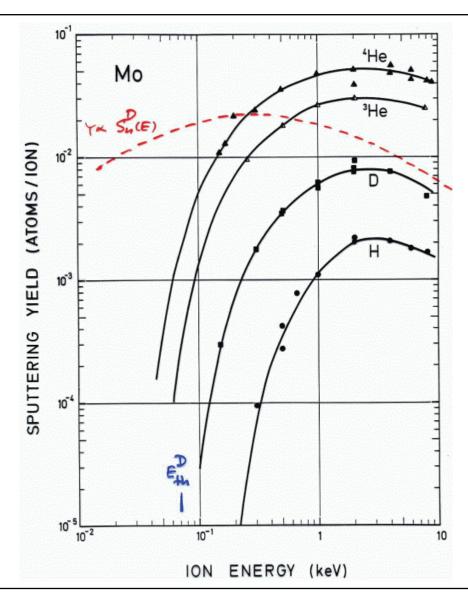
sputtering yield proportional to the energy deposited into collisions near the surface

$$Y(\varepsilon) \propto S_n(\varepsilon)_{x=0}/U_0$$

$$S_n(\varepsilon) = f(M_1, M_2, Z_1, Z_2)Y(\varepsilon)U_0$$

threshold regime

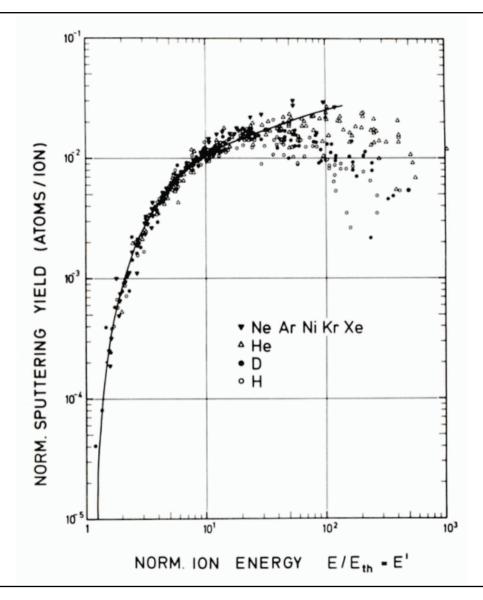




- light ion sputtering in fusion application is dominated by threshold effects
- self-sputtering due to redeposited target atoms can be described by the isotropic collision cascade

Threshold function



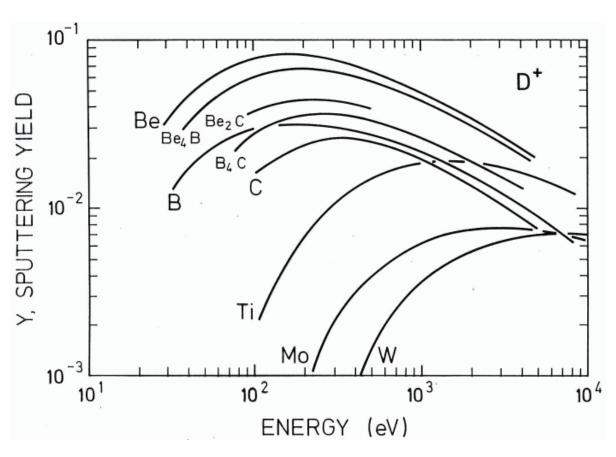


- in the threshold regime all experimental data show a similar energy dependence
- normalized energy scale
 E' = E/E_{th}
- good fit to universal function with

$$Y(E') = (1 - \frac{1}{E'})^{3.5}$$

systematics for light ions

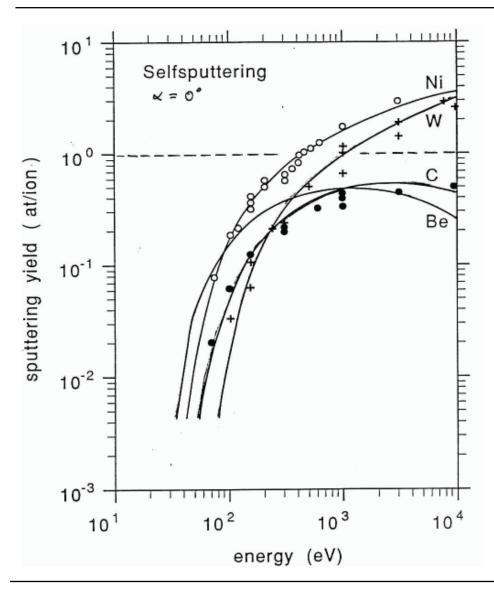




- similar yields in isotropic cascade regime
- strong influence of Z₂ on threshold energy E_{th}

systematics for self-sputtering



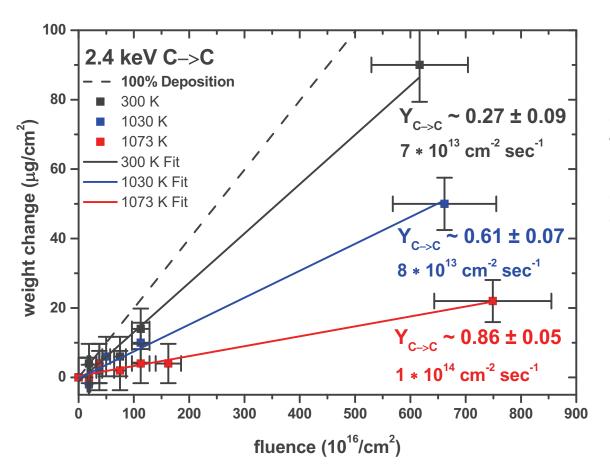


- no dependence of E_{th} on target mass, but on surface binding energy E_s
- strong dependence of yield on mass in isotropic cascade regime due to nuclear deposited energy.
- most important is the yield range close to unity, as runaway impurity production may occur

 $Y_{\text{eff}} = \frac{Y_{\text{D}}}{(1 - Y_{\text{self}})}$

physical sputtering: temperature dependence





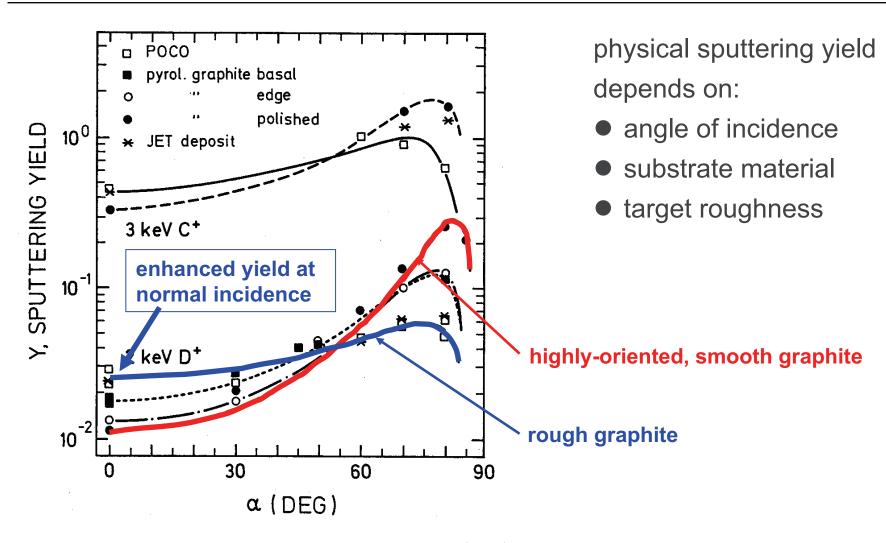
carbon self sputtering as a function of temperature

around 1000 K onset of enhanced sputtering

K. Schmid, J. Roth, J. Nucl. Mater. 313-316, 302 (2003)

physical sputtering: angular dependence





J. Roth, W. Eckstein et al., J. Nucl. Mater. 179-181, 34 (1991)

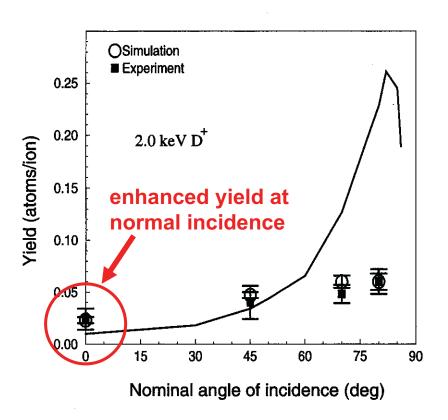
physical sputtering: angular dependence



highly-oriented, smooth graphite

Simulation ■ Experiment 0.25 Yield (atoms/ion) $2.0 \text{ keV D}^{\dagger}$ 0.20 0.15 0.10 0.05 0.00 75 15 30 45 60 90 Nominal angle of incidence (deg)

rough graphite



M. Küstner, W. Eckstein, V. Dose, J. Roth, Nucl. Instrum. Meth. B **145**, 320-331 (2000) The influence of surface roughness on the angular dependence of the sputter yield



- well understood (for the most part)
- key parameter is the surface binding energy E_{SB} (= 7.4 eV for carbon)
- depends on particle energy
- depends on particle mass
- depends on the particle atomic number

energy transfer:

 $T_{\text{max}} = 4 \text{ M}_1 \text{ M}_2 / (\text{M}_1 + \text{M}_2)^2$ \rightarrow isotope effect

- only weakly T dependent
- threshold energy depends on target/projectile combination
- depends on angle of incidence (roughness)



open questions / problems:

- surface binding energy for mixed materials
- accuracy of sputter yields close to the threshold
- sputtering at low energies with molecular ions
 typicall experiments are not performed with D⁺ but with D₂⁺ or D₃⁺ ions instead (higher fluxes) but yields are given per atoms assuming:

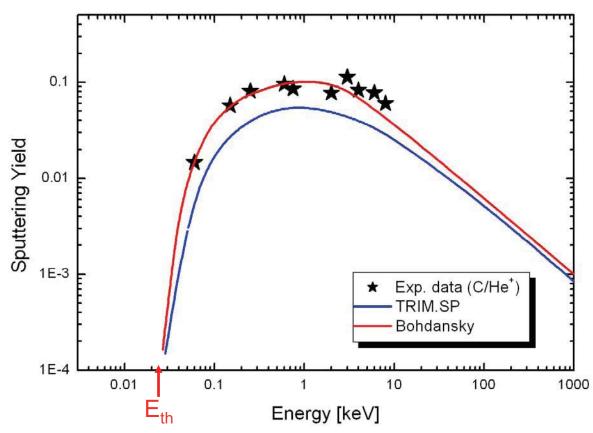
$$j_{D^{+}} = 3 \cdot j_{D_{3}^{+}}$$
 and $E_{D^{+}} = \frac{1}{3} \cdot E_{D_{3}^{+}}$

surely not valid near the threshold!

surface roughness (dynamical development during process)

quantitative description of physical sputtering





the experimental data is fitted with the **Bohdansky** formula:

$$Y = Q.s_n^{TF} \left(1 - \left(\frac{E_{th}}{E_o} \right)^{\frac{2}{3}} \right) \left(1 - \frac{E_{th}}{E_o} \right)^2$$

$$S_n^{TF} = S_n^{TF}(\varepsilon)$$

$$\varepsilon = E_o \frac{M_{t \arg et}}{M_{ion} + M_{t \arg et}} \cdot \frac{a_L}{Z_{ion} \cdot Z_{t \arg et}}$$

$$Q = 0.169 \ [atoms/ion]$$

$$E_{th} = 25,4 \ [eV]$$

J. Roth, E. Vietzke, A.A. Haasz; Atomic and Plasma-Material Interaction Data for Fusion, Suppl. to Nuclear Fusion 1 (1991) 63.

C. Garcia-Rosales, W. Eckstein, J. Roth; J. Nucl. Mater. 218 (1994) 8-17.

quantitative description of physical sputtering



Monte Carlo Simulations based on the binary collision approximation

- calculating asymptotic trajectories of consecutive collisions between projectile and target atoms
- continuous drag by electronic stopping
- randomly choosing the distance to the next collision partner, the collision parameter, and the azimuth.
- following the projectile and all colliding target atoms that received a certain minimum energy

quantitative description of physical sputtering



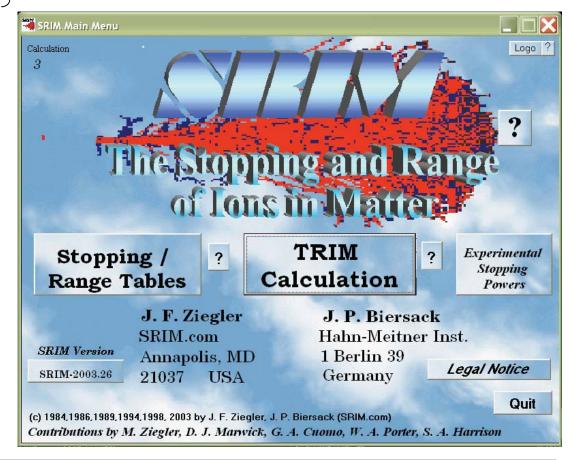
TRIM (transport of ions in matter)
TRIM.SP (sputtering)
TRIDYN (dynamic TRIM)

SRIM (see www.srim.org)

see exercise

:

SDTrim available via SDTrimSP@ipp.mpg.de



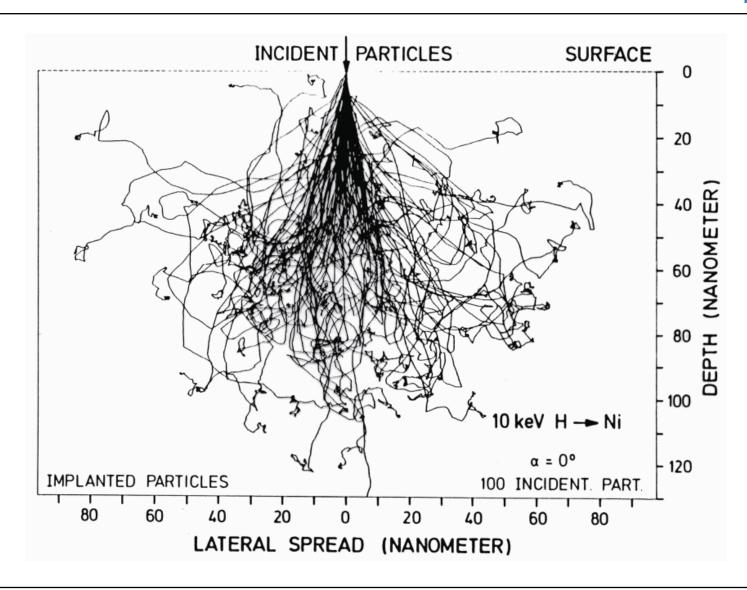


some remarks on TRIM and its derivates

- revery powerful tools in describing the collision cascades for nearly every projectile on every target atom out of the elemental table
- they are not ab initio calculations but include fit parameters to describe experimental data like
 - surface binding energy
 - displacement energies
- do not include chemistry effects (bonding of H in C)
- > do not include diffusion effects
- often do not change the layer composition (TRIDYN does)

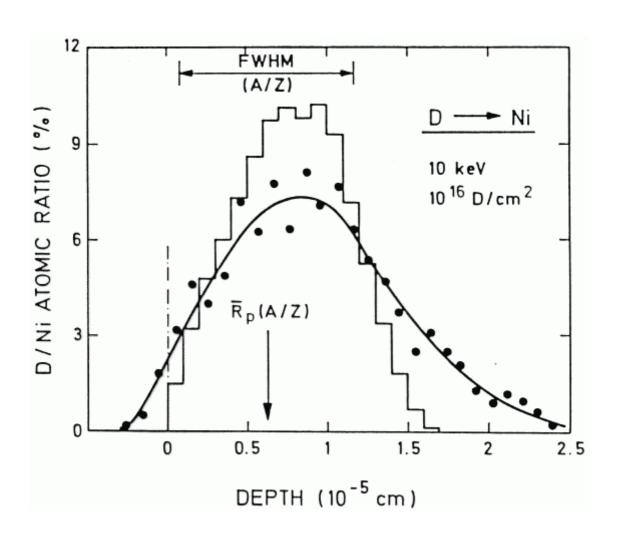
collision cascade

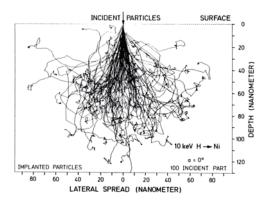




range and range distribution

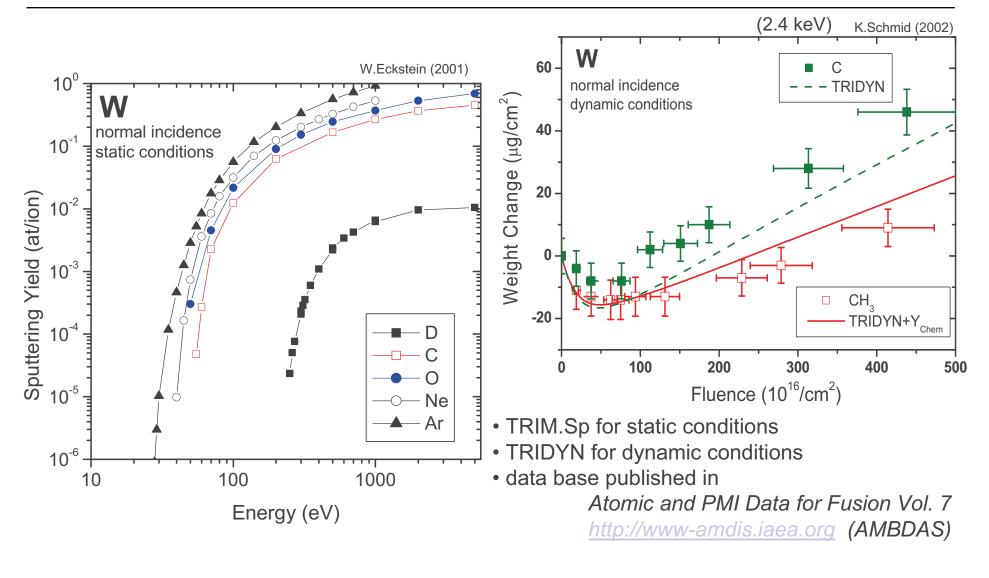






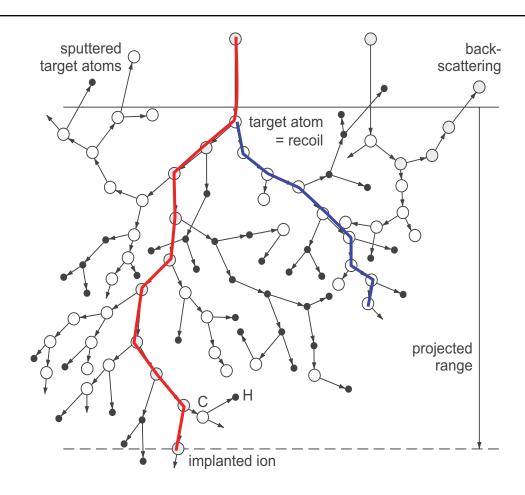
sputtering by non-recycling ions





physical sputtering: projectile-solid interaction





*W. Eckstein, 'Computer Simulations of Ion-Solid-Interactions', Springer-Verlag (1991)

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

schematic representation of C impinging on a-C:H

relevant processes:

- sputtering
- implantation
- backscattering
- displacement
- activation

open questions:

- what happens with displaced hydrogen?
- how to incorporate the chemical nature of hydrogen

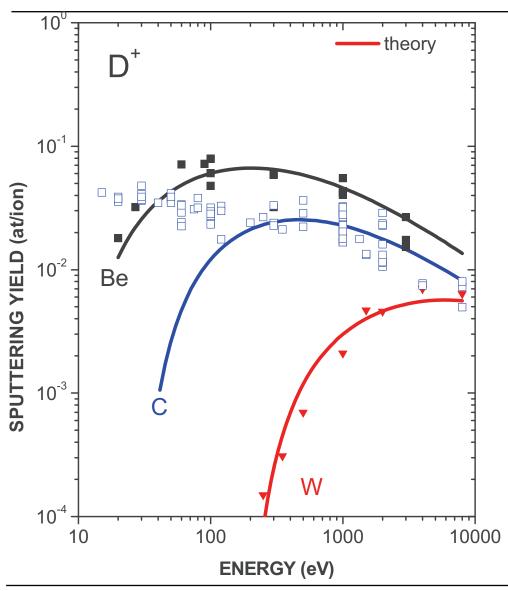
physical sputtering



- Physical sputtering is the kinetic ejection of surface atoms by incident energetic ions or atoms due to collision processes (playing pool with surface atoms).
- As surface atoms can escape only if it receives an energy larger than the surface binding energy, a threshold energy for the incident particles is required.
- In fusion application sputtering by hydrogen and helium ions and atoms is important, but also the self-sputtering due to returning impurity atoms.

erosion at room temperature

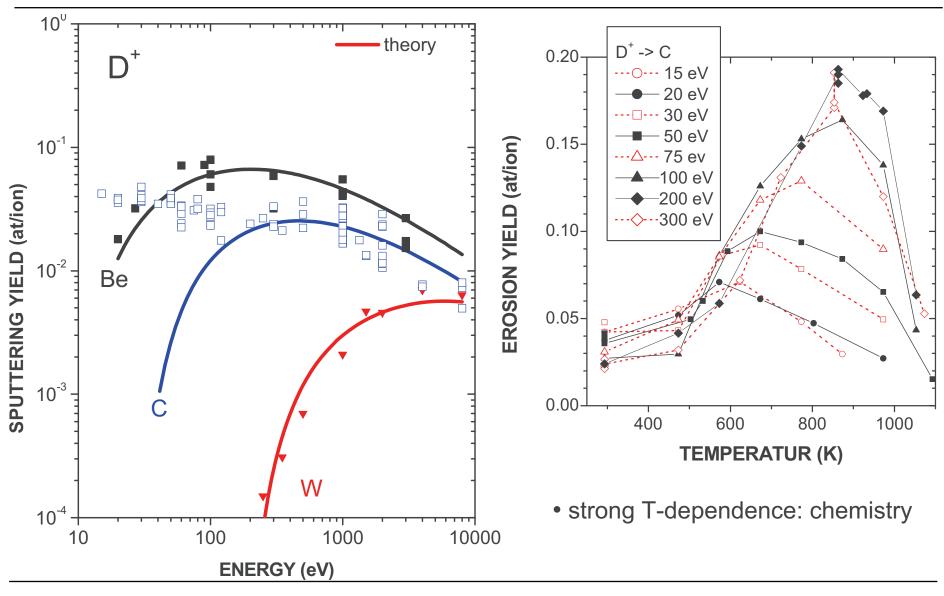




- advantage for high-Z materials
- strong deviation for Carbon based materials
 - ⇒ chemical effect?

erosion of plasma-facing materials





nomenclature



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erosion of graphite by energetic hydrogen



it is not chemical erosion

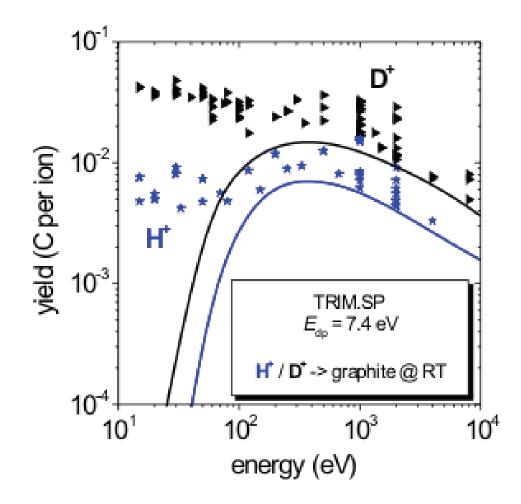
H⁰ at T > 400 K with a max. at ≈ 650 K – 800 K

it is not physical sputtering

energetic ions $E > E_{th}$ no chemistry

but its chemical sputtering

hydrogen ions, low-T, low-E



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

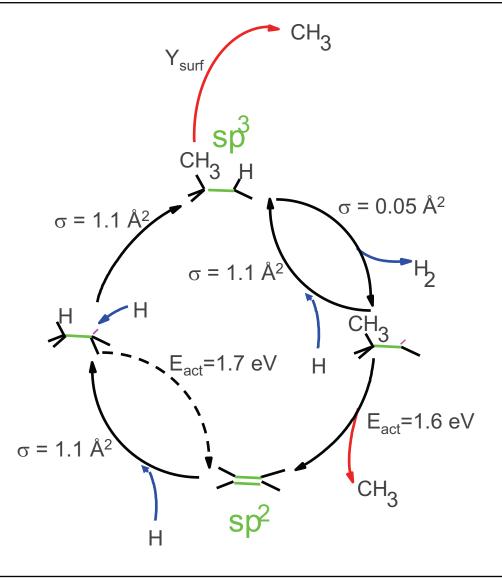
chemical sputtering: one attempt



hydration and erosion circle:

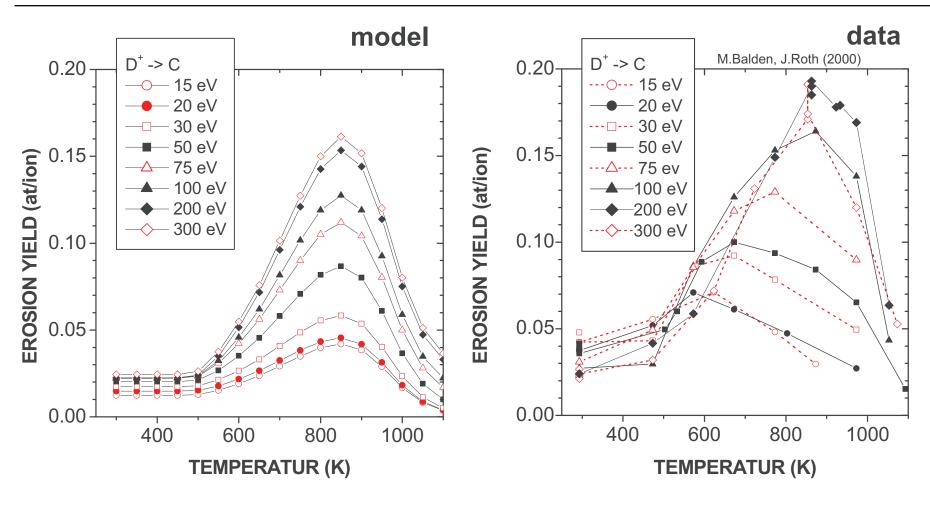
A. Horn et al., Chem. Phys. Lett. 231, 193 (1994) J. Roth, J.Nuclear Mat. 266-269, 51 (1999)

 Ion induced release of weakly bound hydrocarbon radicals complexes from the surface



chemical erosion at elevated temperatures





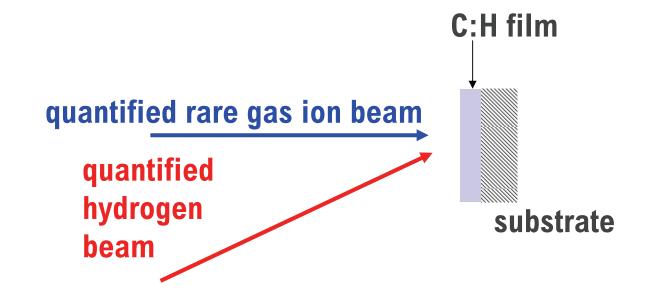
- adequate modeling of erosion
- · does not explain shift oft maximum with energy



Quantified particle-beam experiments: separating physics from chemistry

measuring erosion yields





erosion yield =

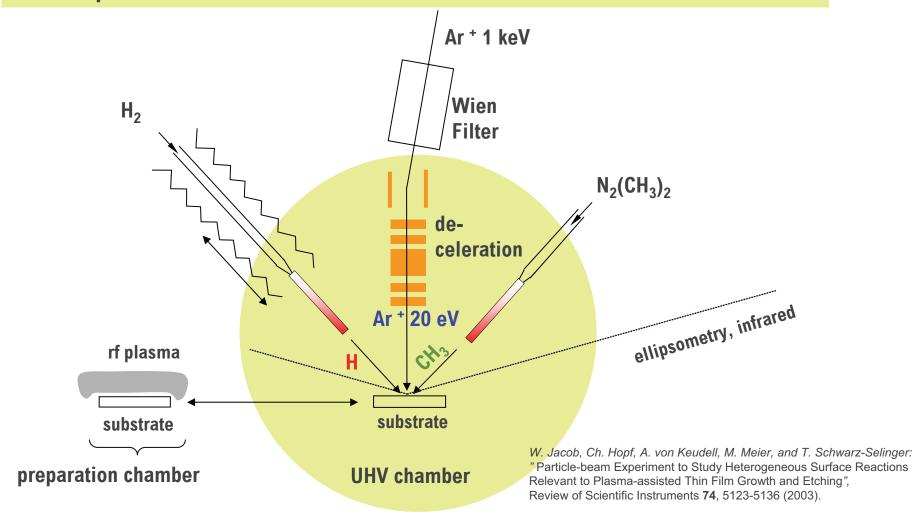
measured erosion rate in eroded carbon atoms per cm⁻²s⁻¹

impinging ion flux per cm⁻²s⁻¹

quantified particle-beam experiments

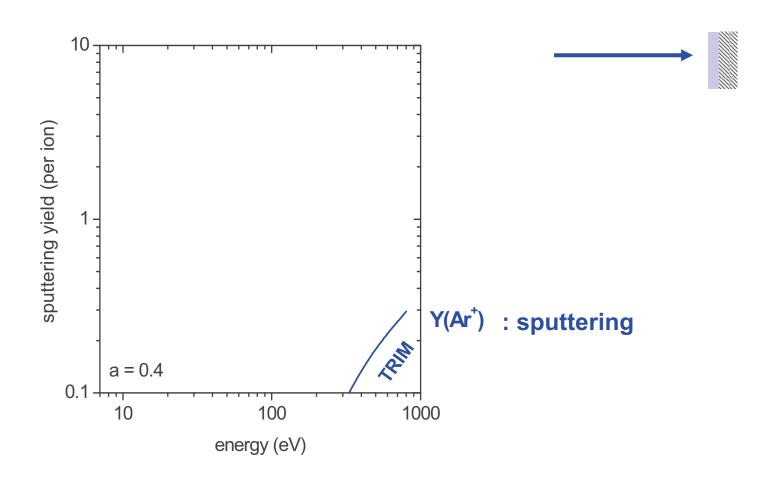


UHV experiment with 2 radical beam sources and one ion beam source



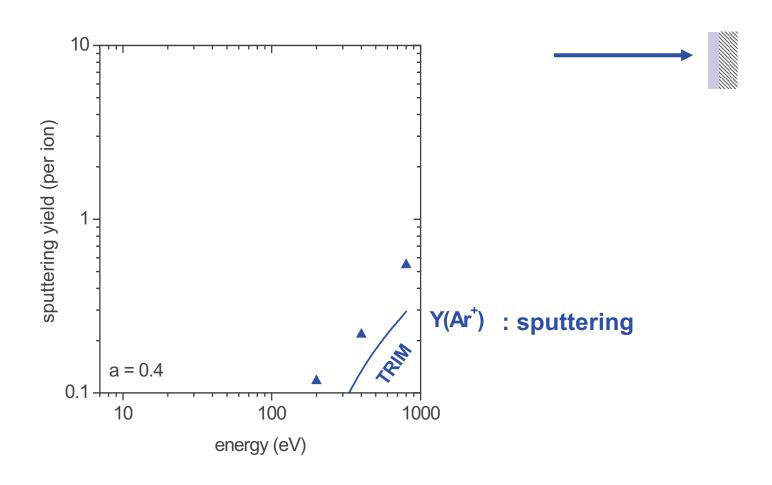
physical sputtering



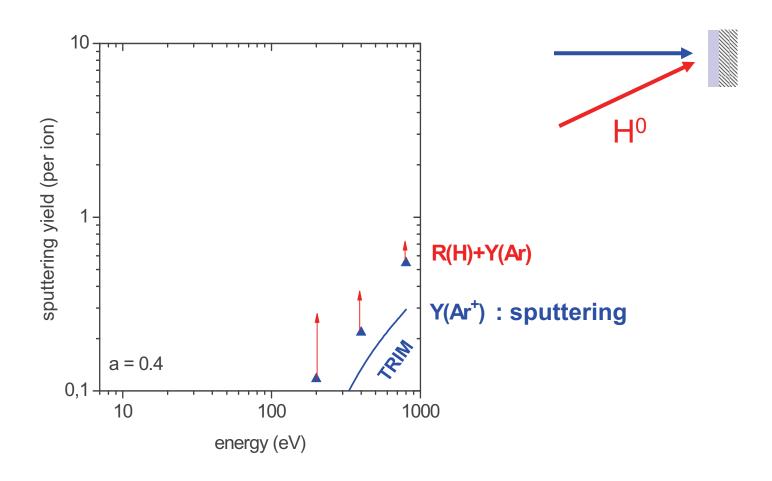


physical sputtering

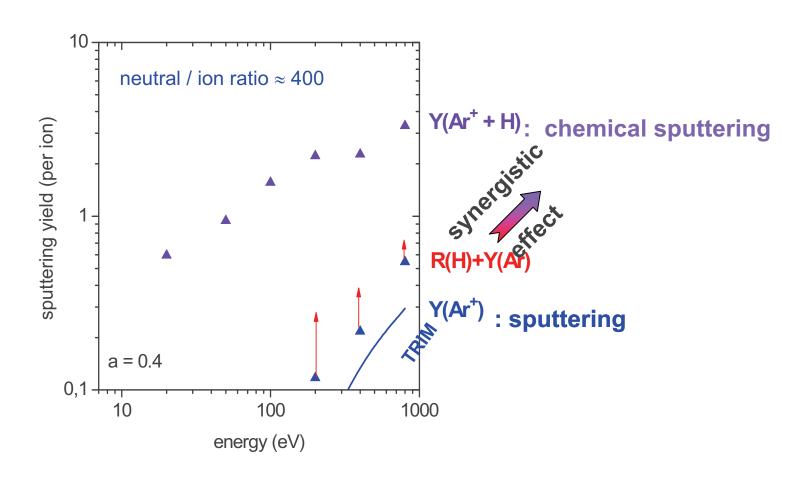




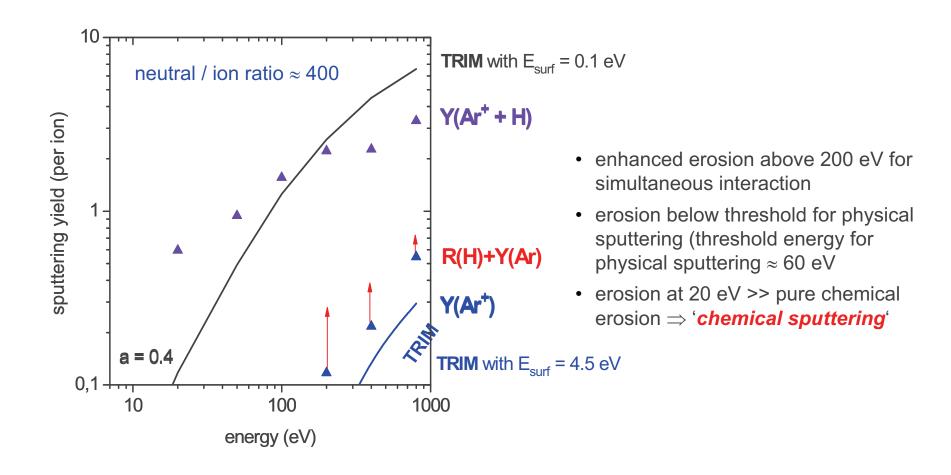




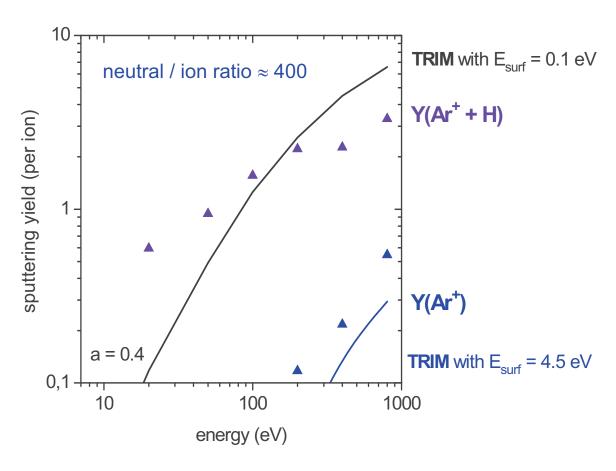








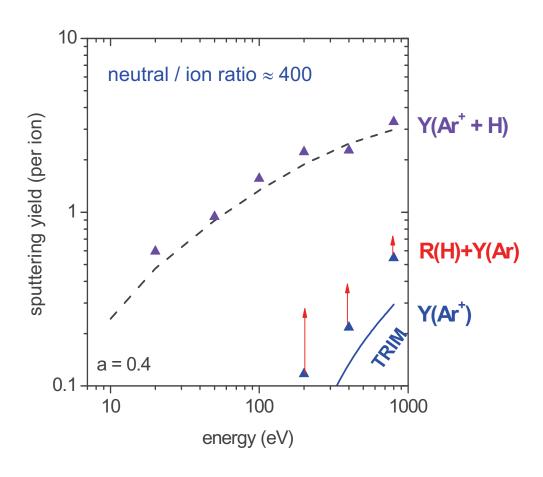




sputtering of weakly bound surface radicals seems not to be physical

chemical sputtering

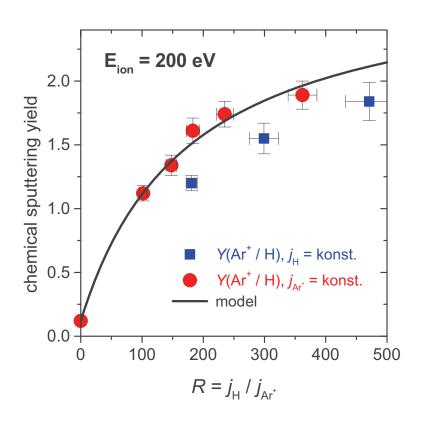




model for chemical sputtering

Ar⁺|H flux dependence





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

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

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

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

Fit parameters:

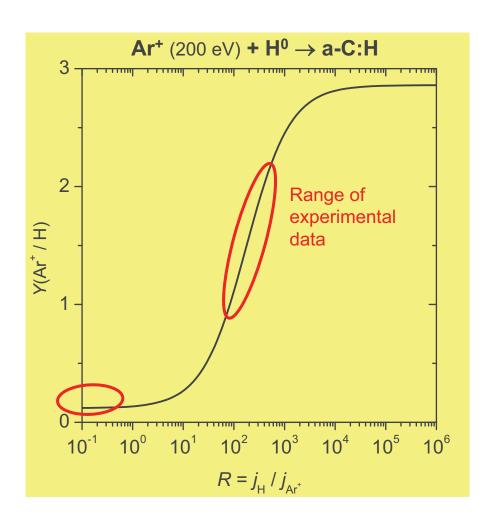
$$S = 176$$

$$Y_{chem} = 2.86$$

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

Ar⁺|H flux dependence

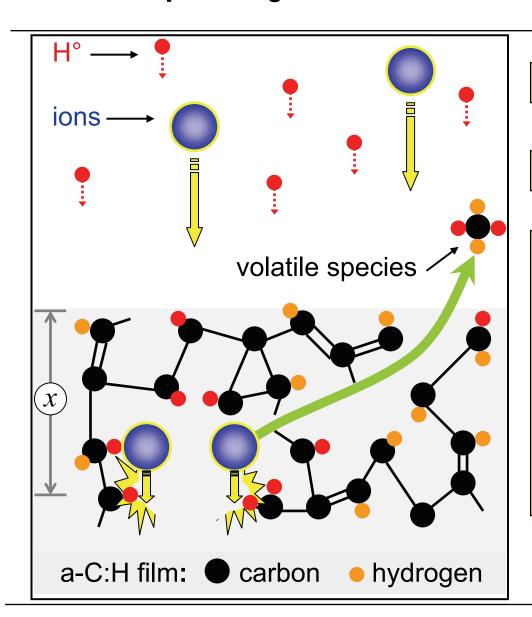




Saturation requires much more H than ions (R > 1000)

chemical sputtering mechanism





1. ions break C-C bonds

2. H° passivates broken bonds

Repetition of 1 and 2

→

3. volatile hydrocarbons

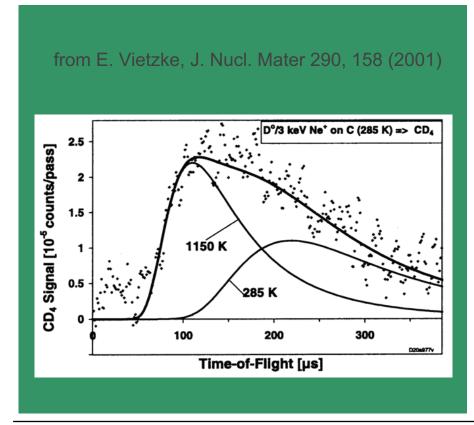
diffusion to the surface

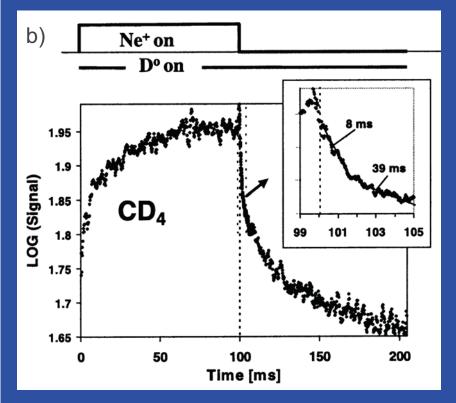
desorption

supporting results from literature



- 1. CH₄ main (C₁-) erosion product (Vietzke et al. J. Nucl. Mater. 128&129, 545 (1984))
- 2. energy distribution of erosions products
- 3. time delay between end of ion bombardment and end of particle release





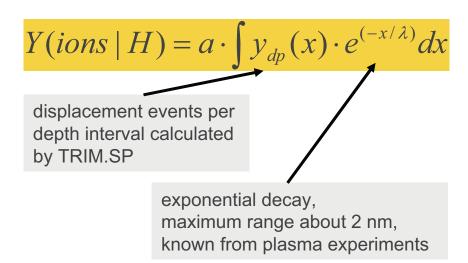
chemical sputtering model



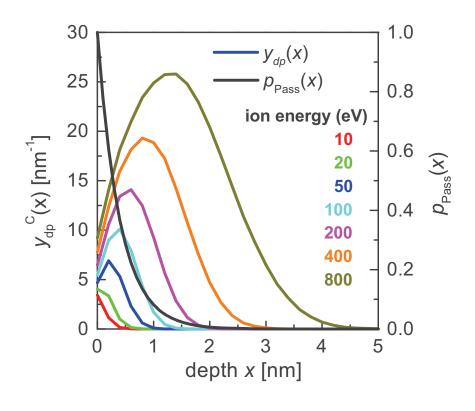
$$Y(ions \mid H) \propto \int y_{bb}(x) \cdot p_{pass}(x) dx$$

bond breaking due to ion impact

passivation by atomic H



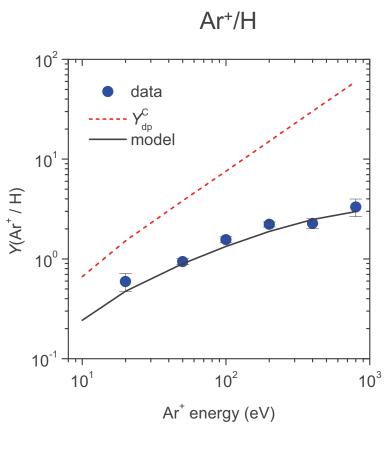
a is a fit parameter



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

energy dependence



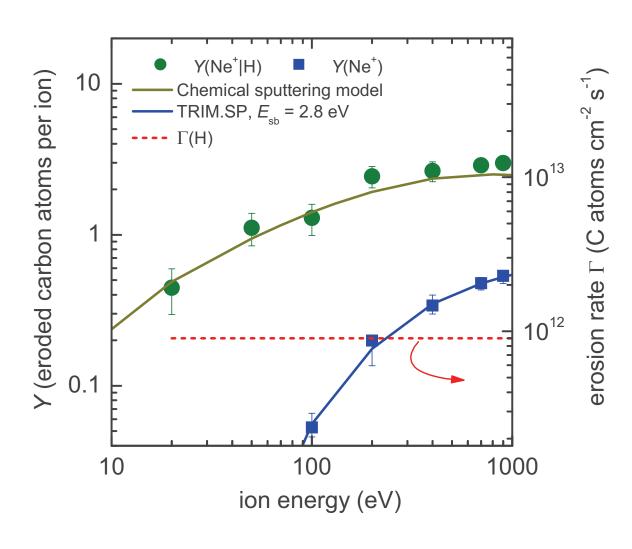


$$a = 0.4$$

$$j_{H}$$
 = 1.4×10¹⁵ cm⁻² s⁻¹, j_{Ar+} = 3.6×10¹² cm⁻² s⁻¹, R = $j_{H/}j_{Ar}$ \approx 400

: Ne+ H

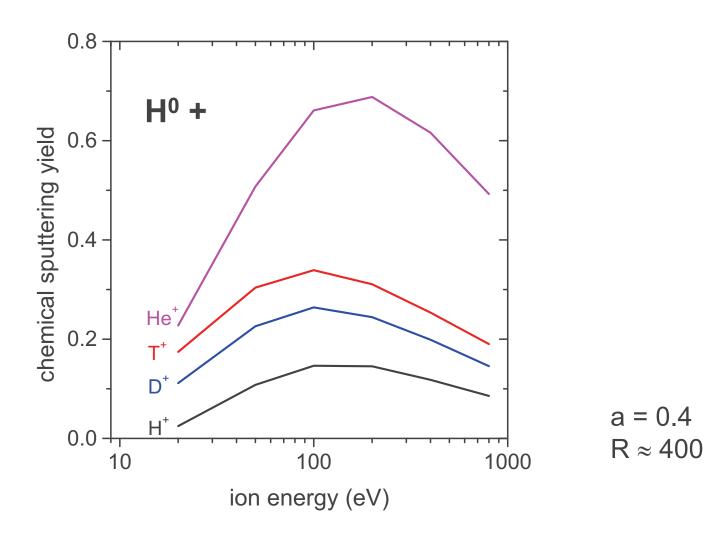




- Excellent agreement between model and data (same parameters as for Ar, i.e., a = 0.4))
- yield > 1 for E_{ion} >50 eV

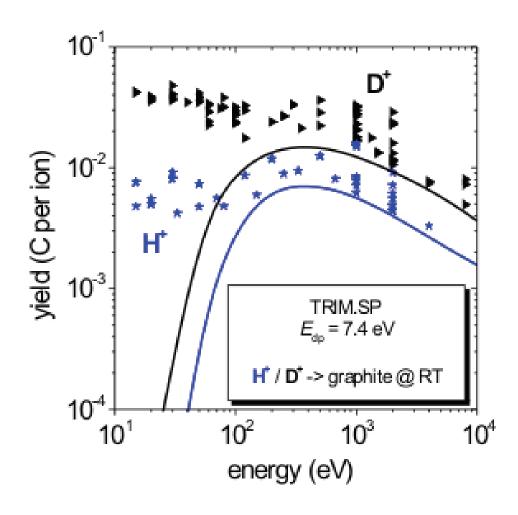
energy dependence: modeling results





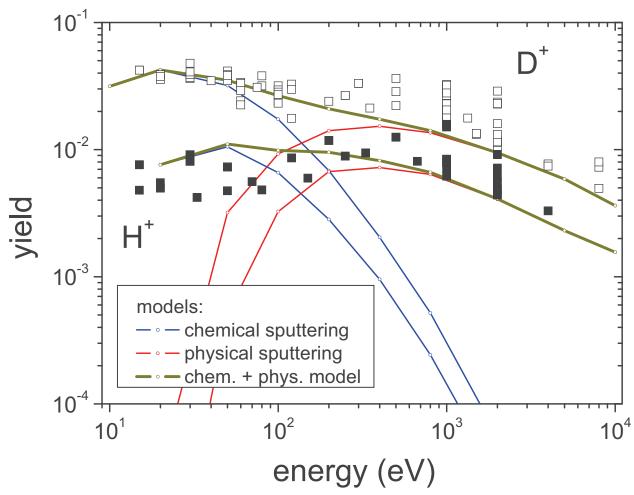
erosion of graphite by energetic hydrogen





chemical sputtering with reactive ions





C. Hopf and W. Jacob 2005

chemical sputtering with reactive ions



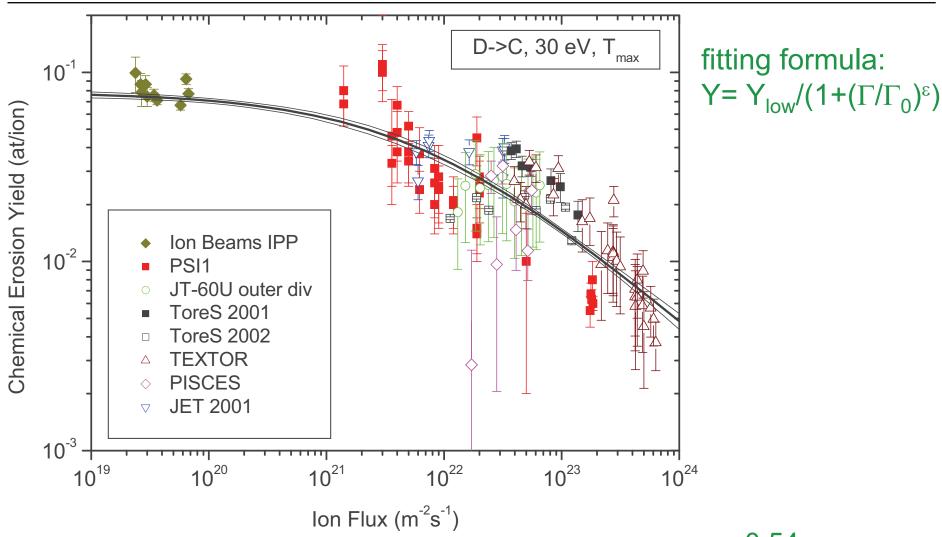
total yield = chemical sputtering + physical sputtering
$$Y(E) = \int y_{\rm dp}^{\rm C}(x,E) \, n(x,E) \exp(-x/\lambda) \, {\rm d}x + Y_{\rm phys}(E)$$

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

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

erosion (Chemical sputtering) at high ion fluxes





results from fitting: $Y_{Tmax}(\Gamma) = 0.79/(1 + (\Gamma/6x10^{21})^{0.54})$

Summary on erosion



- 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, N₂, ...
- temperature dependence of the erosion maximum not understood
- decrease in erosion rate at high fluxes not under stood

exercise 2



• Use SRIM to compute the energy dependence of the physical sputtering yields for D⁺ on tungsten and carbon, as well as the self-sputtering yields.

• Evaluate the threshold energies for D⁺ sputtering of tungsten and of carbon.

At what energy does the self-sputtering yield equal unity in these two cases.

• compare the yield for D⁺ on carbon with the yield for D⁺ on a thin (5 nm thick) carbon film on tungsten for an energy of 1 keV. Why is it so different?