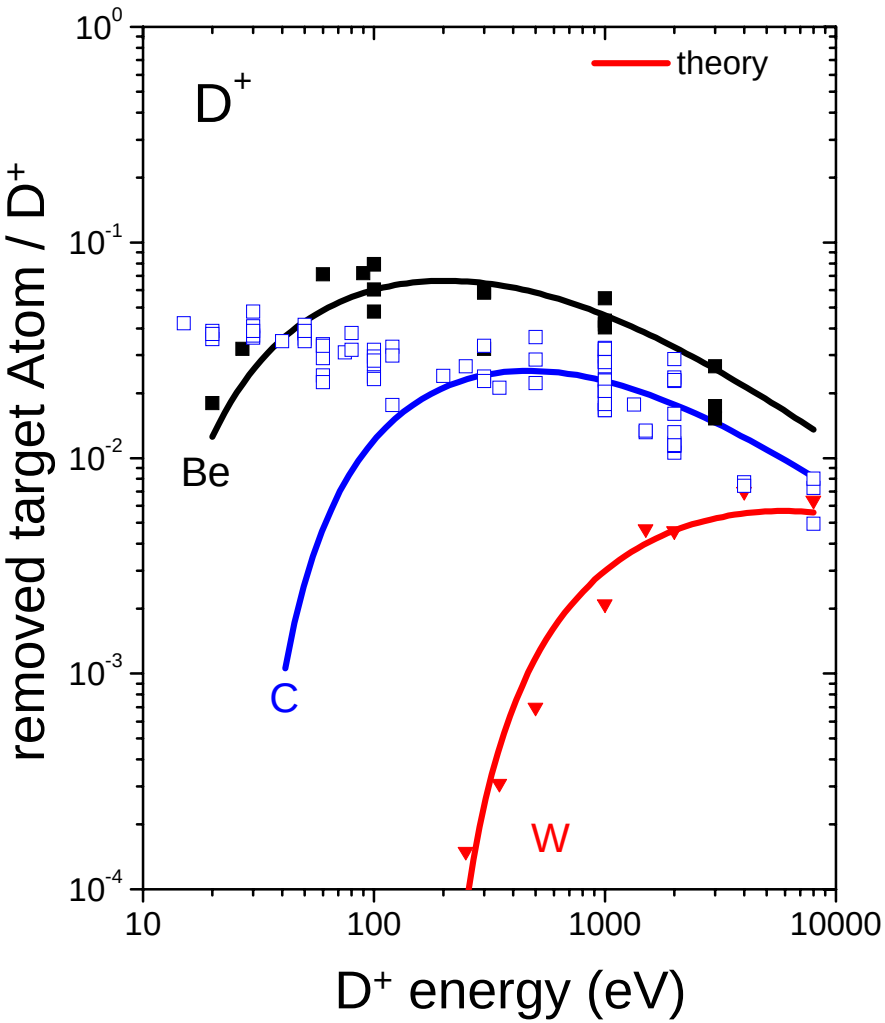
Thomas Schwarz-Selinger

Erosion Processes (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 between D and C forming volatile hydrocarbons

Research groups: 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

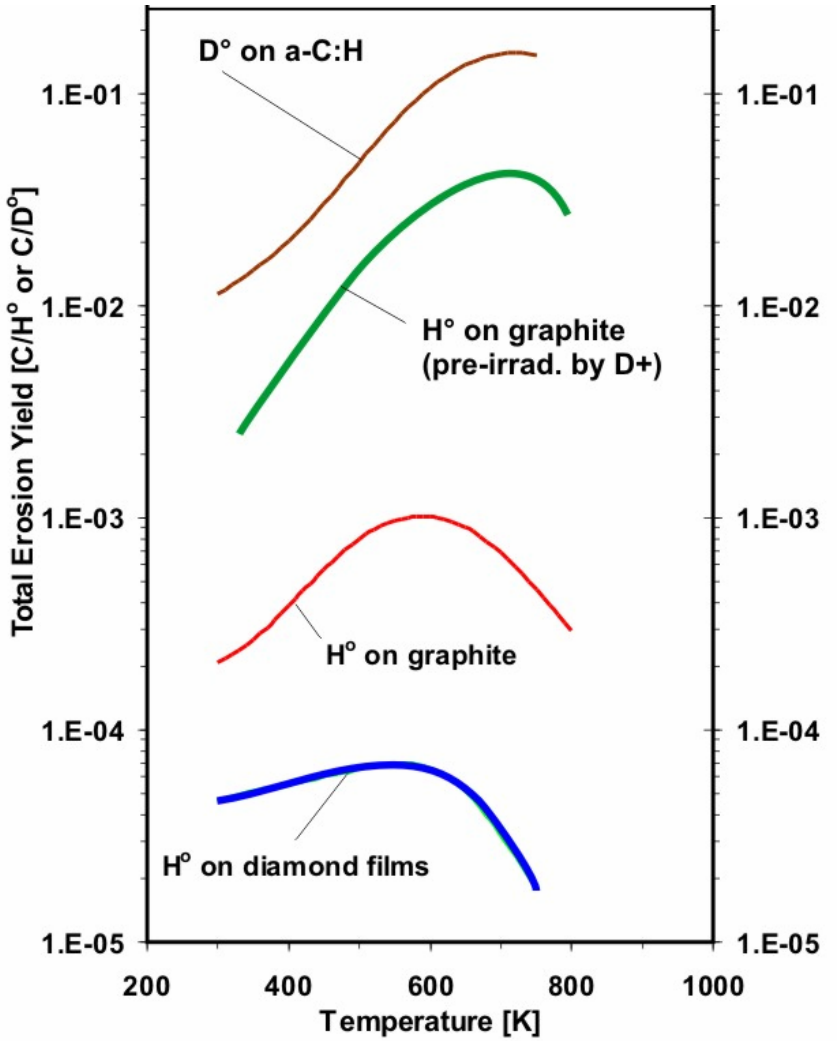
Nomenclature

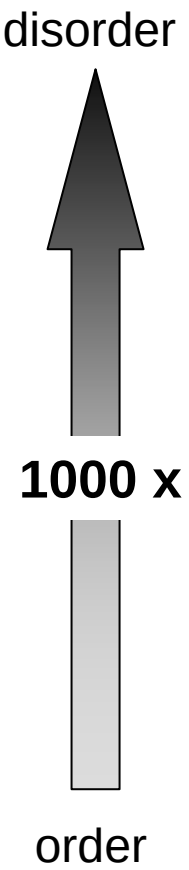
- **Chemical erosion** is a selective removal of surface atoms by ***chemical reactions***, forming volatile reactants that can desorb.

- **Physical sputtering** is the ***kinetic ejection of surface atoms*** by incident energetic ions or atoms ***due to collision processes***. (playing billiards with surface atoms).

- **Chemical Sputtering** 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: structure dependence





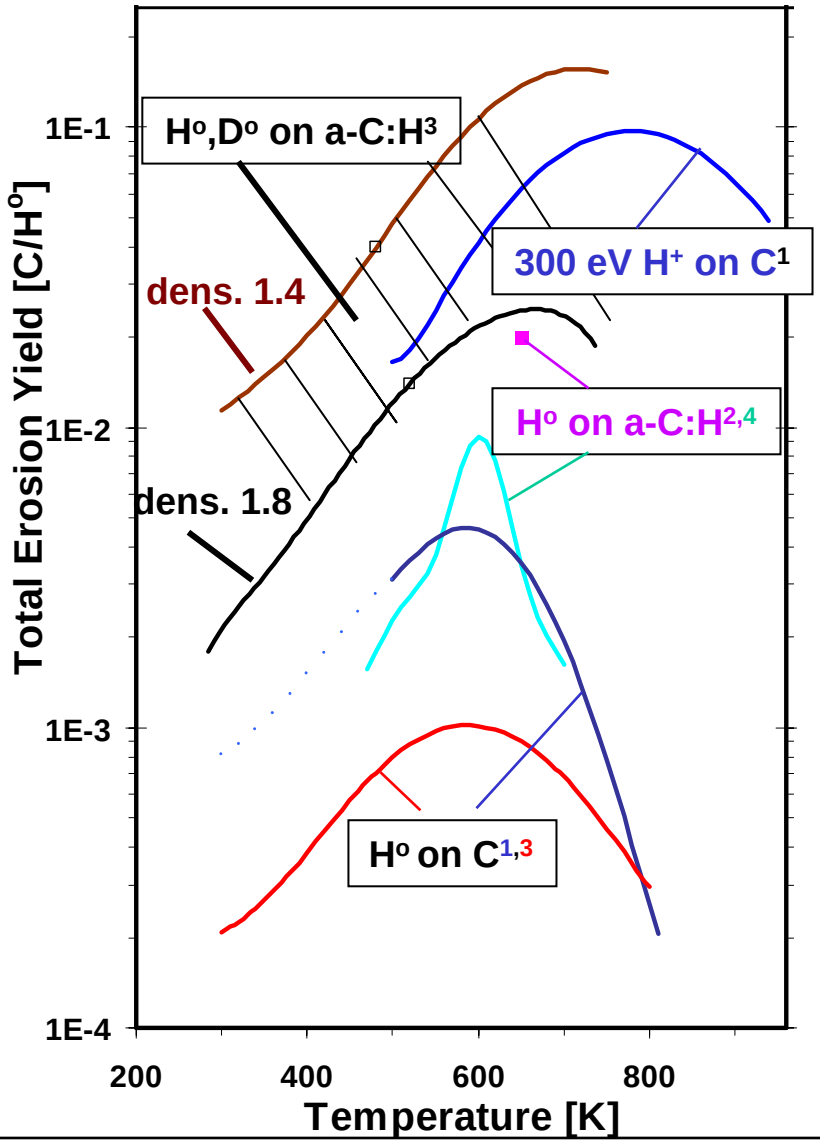
Total Y of H^o on films of:

- a-C:H (plasma-deposited),
- pre-irradiated graphite,
- graphite and
- diamond

- **reactivity of the surface depends critically on the surface structure**

E. Vietzke et al., Surf. Coat. Technol. ***47*** *(1991) 156-161*

Chemical erosion: structure dependence



- The erosion yield of H^o on a-C:H reach values of the maximum of H^+ on C
- Good agreement of a-C:H(hard): black curve and Schwarz-Selinger calibration point, less compared to Horns curve.

1. J.W. Davis et al., JNM 155-157(1988)243
2. T. Schwarz-Selinger.et al., J. Vac.Sci.Techn. A18 (2000) 995
3. E. Vietzke et al. Fus. Technol. 15 (1989) 108
4. A. Horn et al., Chem. Phys. Lett. 231 (1994) 193

Chemical Erosion: microscopic model

Hydration and erosion circle:

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

1) chemisorption of H on sp^2 site

2) chemisorption of H on sp^x site (hydration)

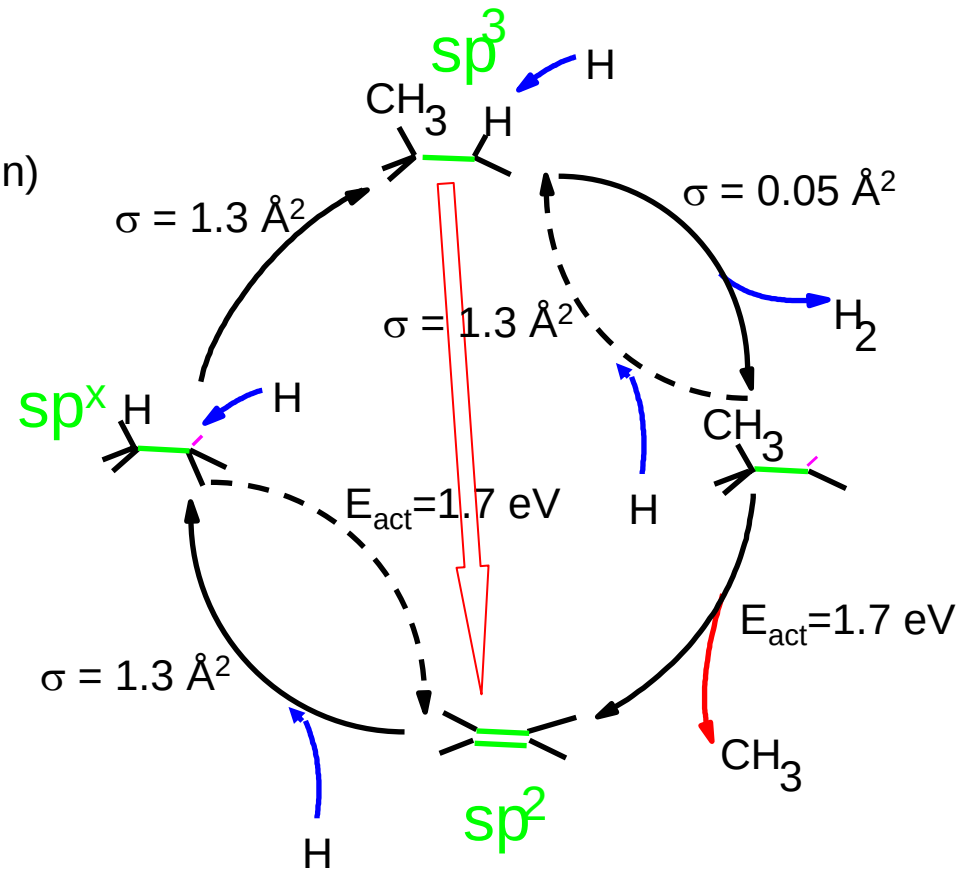
3) abstraction of H to form H_2

4 a) thermal release of CH_3 radicals from activated sites above 400 K

4 b) chemisorption of H on sp^x site

5) relaxation back to sp^2 above 750 K

6) direct thermal decomposition to sp^2 above 900 K with E_{act}=2.4 eV



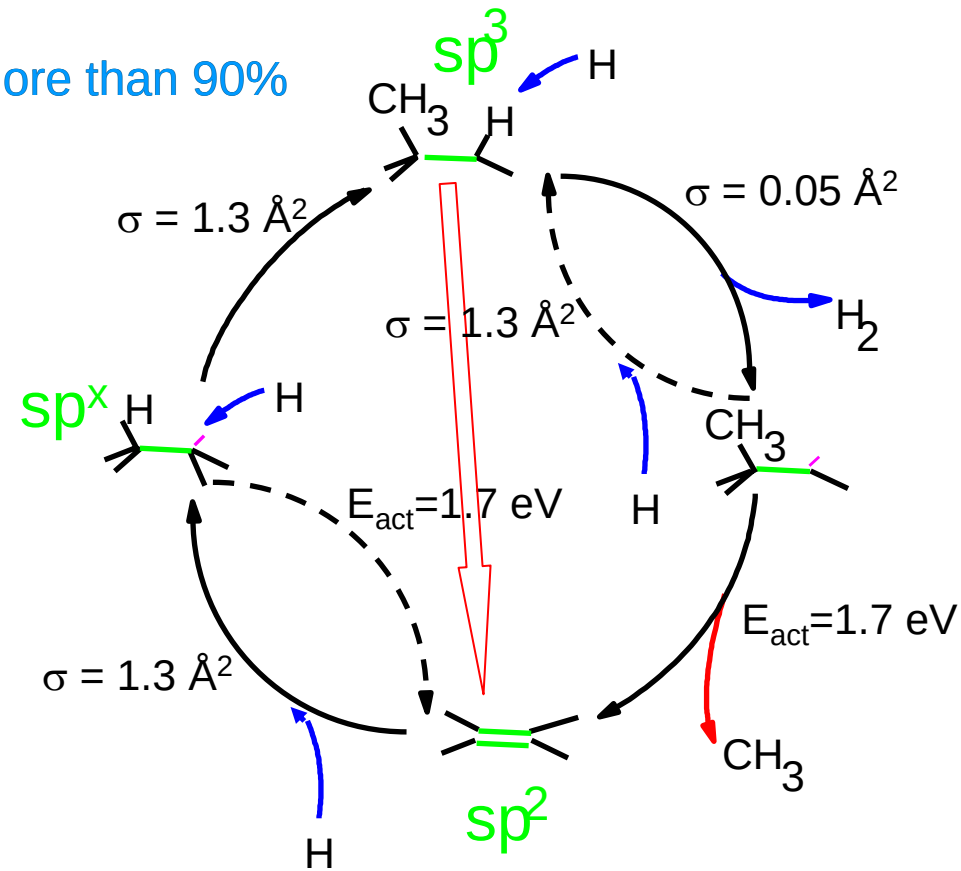
Chemical Erosion: microscopic model

Hydration and erosion circle:

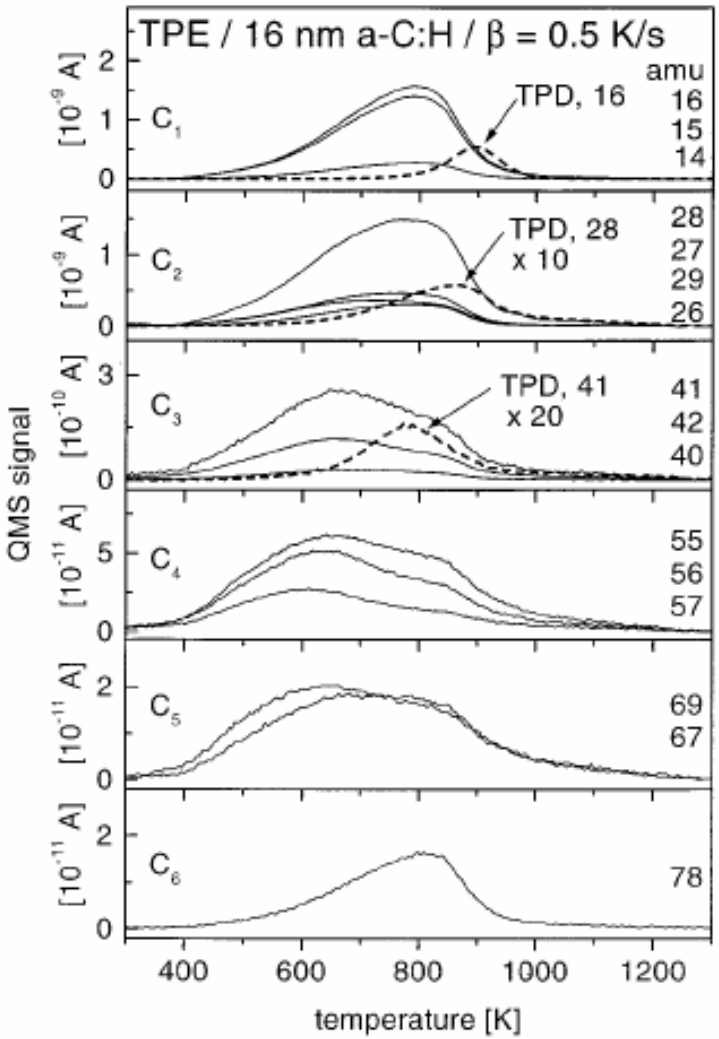
Horn et al., Chem. Phys. Lett. 231, 193 (1994)
Zecho et alJ. Phys. Chem. B 105 (2001).

- hydration at room temperature of more than 90% of all possible adsorption sites
- erosion maximum
- flux dependence of the erosion maximum

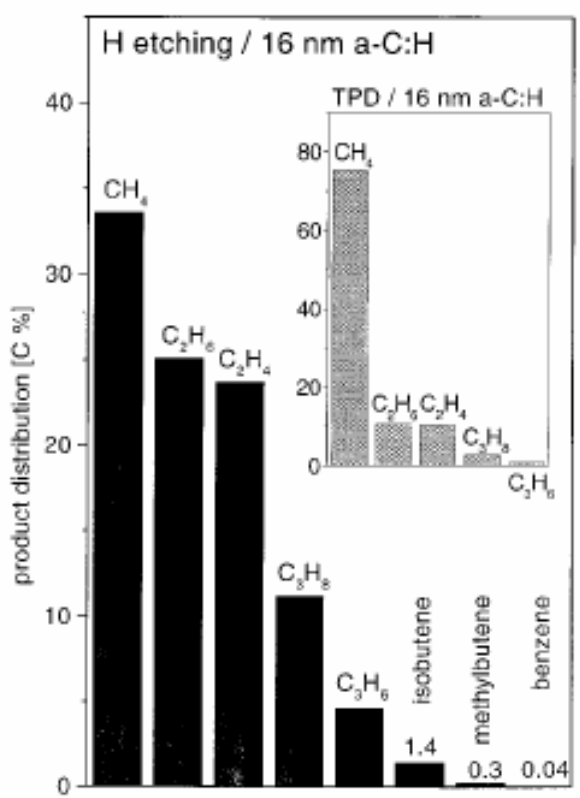
600 K at 10^{17} $m^{-2}s^{-1}$
750 K at 10^{20} $m^{-2}s^{-1}$
??? K at 10^{24} $m^{-2}s^{-1}$ (ITER)



Chemical erosion: product distribution



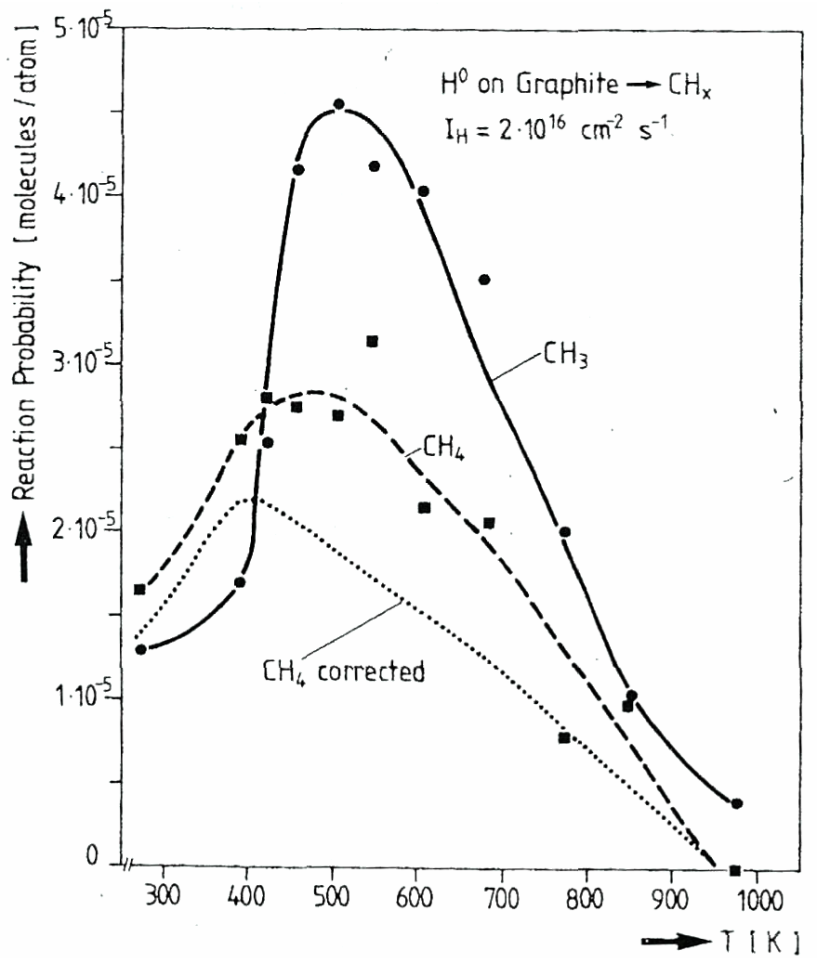
Formation of volatile C_xH_y:
Thermal ***decomposition*** and ***erosion with H^o*** of dense a-C:H film



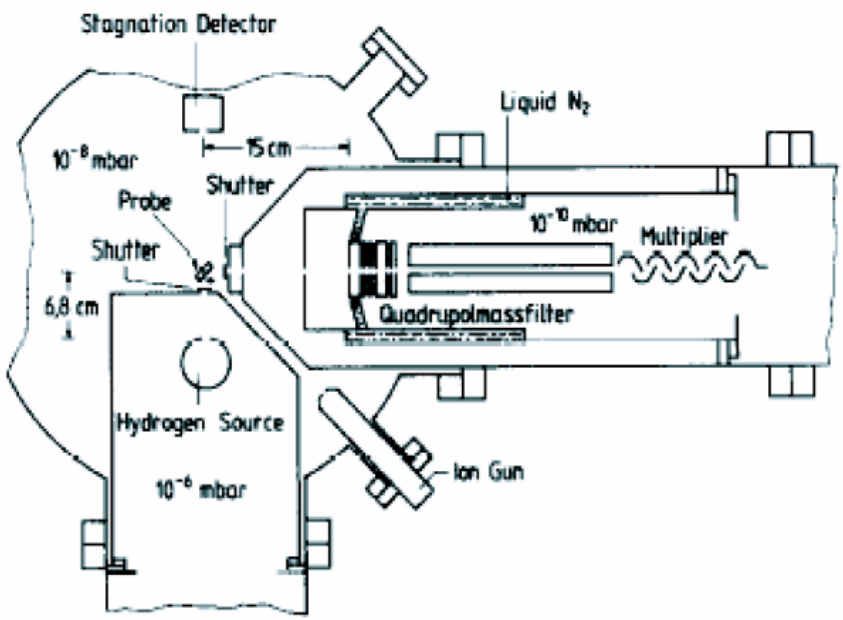
*T. Zecho, B. D. Brandner, J. Biener, J. Küppers; J. Phys. Chem. B **105** (2001) 6194-6201*

Chemical erosion: direct identification of the precursor

At T=500K → ratio CH_3/CH_4 ~ 2



dedicated experiment to detect reactive products:

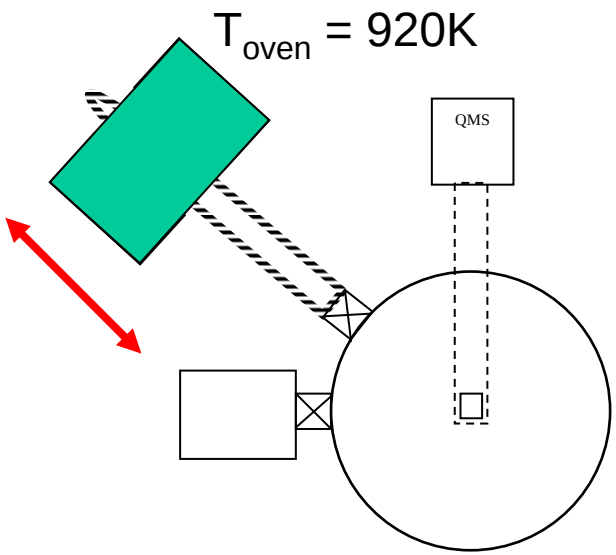


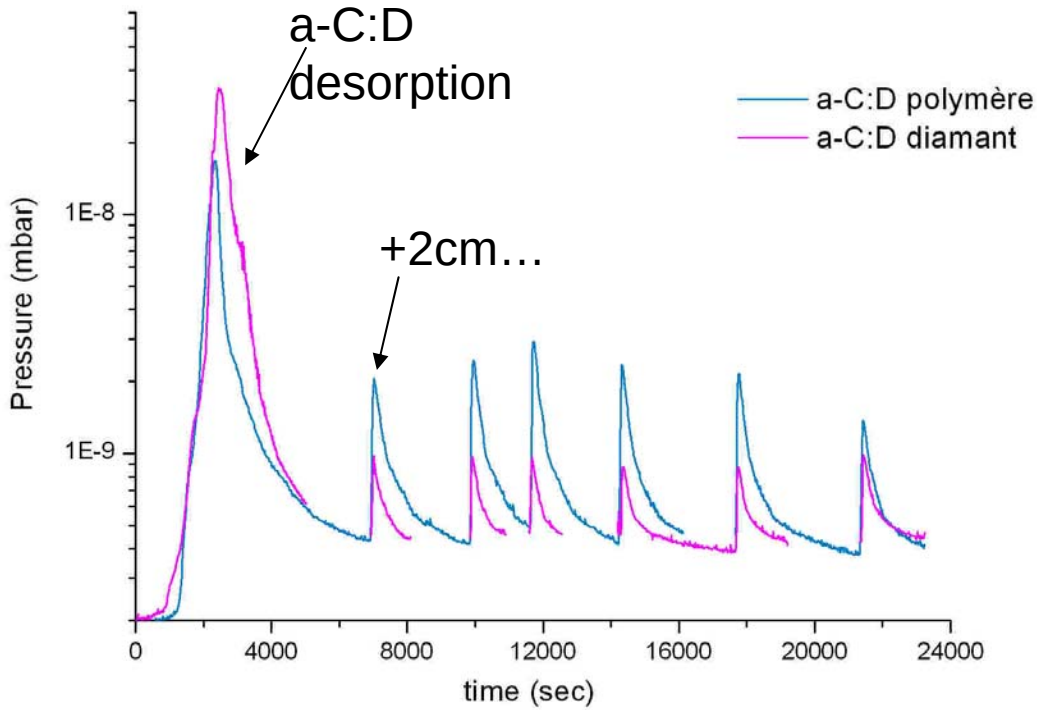
E. Vietzke, K. Flaskamp, V. Philipps.; J. Nucl. Mater. ***128-129*** *(1984) 545-550*

Chemical erosion: product distribution

what about soft a-C:H (polymerlike):

Redeposition!





Oven displacement : Redeposition on the wall of the quartz tube

Soft a-C:D : ~50% of the initial desorption

Hard a-C:D : <10% of the initial desorption

Chemical Erosion: Present Status

erosion of dense a-C:H

- Precursor for chemical erosion is a CH_3 group (C_2H_x) adjacent to a dangling bond site
  (both are produced by interaction with atomic hydrogen)
- cross section for hydrogenation and abstraction and threshold energies for relaxation are known
- nearly all eroded material is transferred into none-reactive volatile products
- shows no isotope effect

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

- high flux limit of the model
- impact of vibrationally excited molecules on erosion?

Nomenclature

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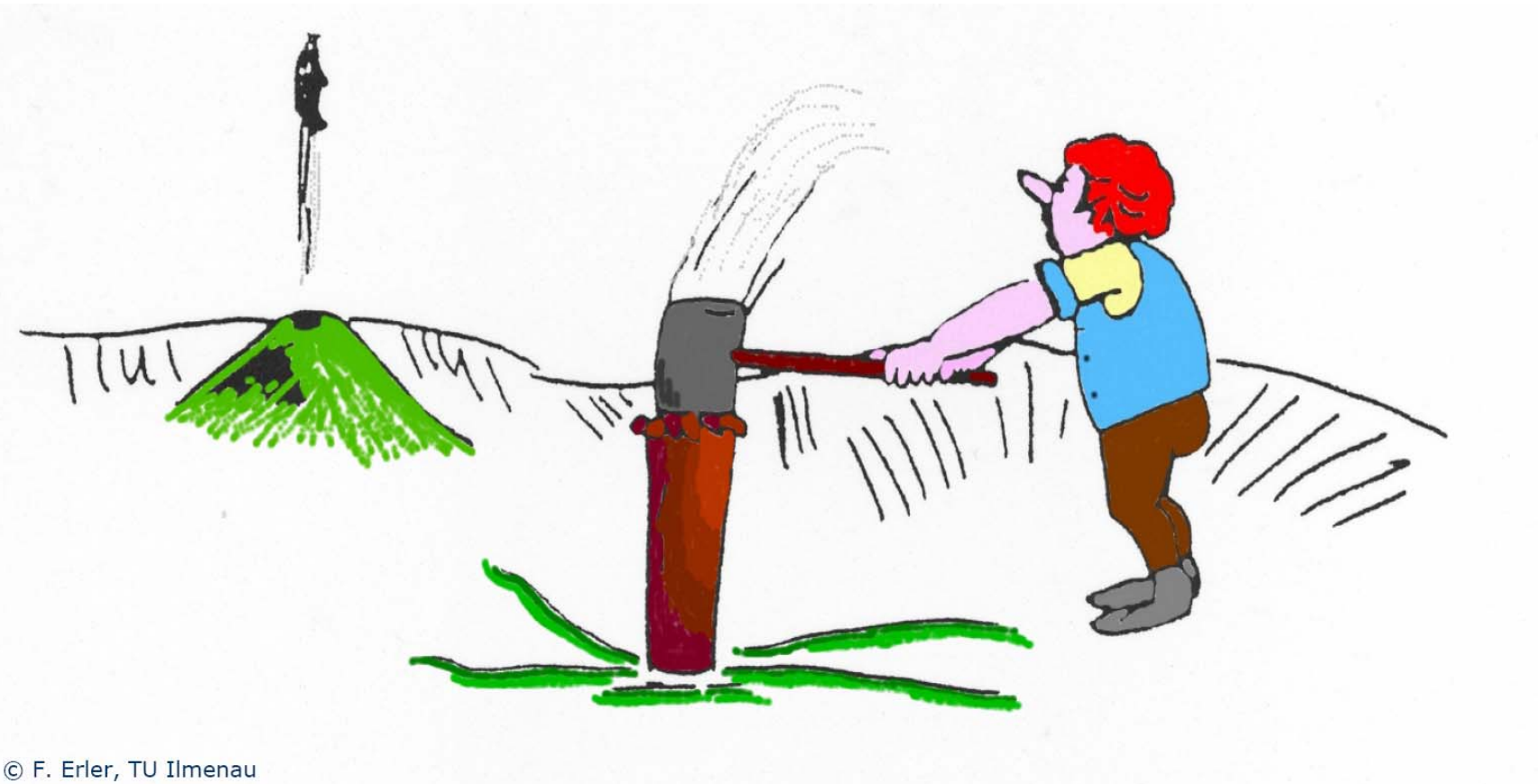
- **Physical sputtering** is the ***kinetic ejection of surface atoms*** by incident energetic ions or atoms ***due to collision processes***. (playing billiards with surface atoms).

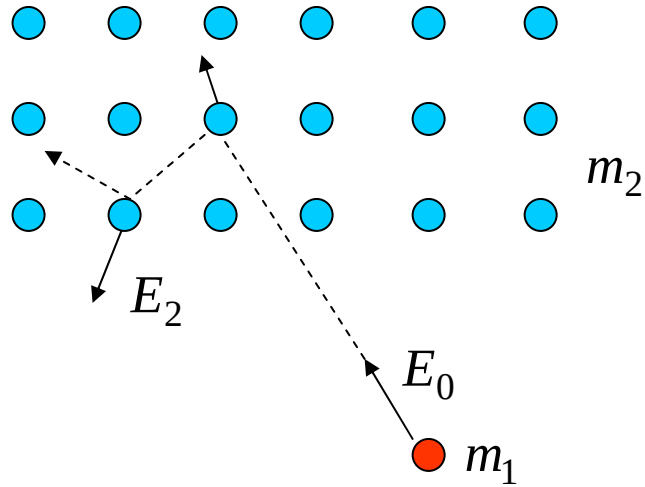
- **Chemical Sputtering** is a process whereby ***ion bombardment causes or allows a chemical reaction to occur*** which produces a particle that is weakly bound to the surface and hence easily desorbs in the gas phase.

Physical Sputtering



Physical Sputtering

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



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

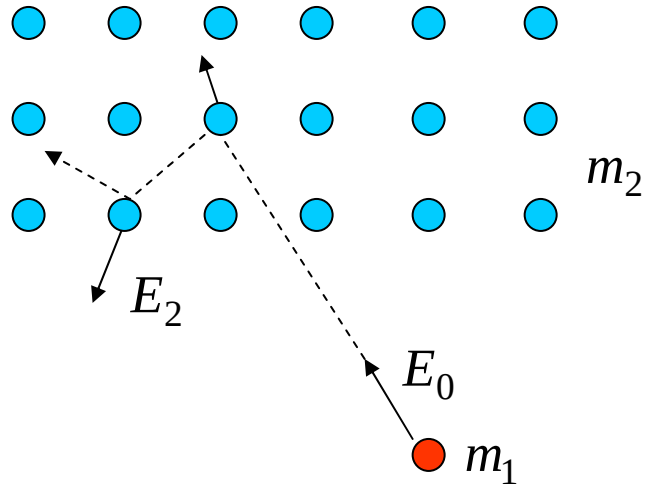
$$m_1 < m_2\,, \text{ after first collision}: E_1 = E_0(1-\gamma)$$

$$\text{transfered energy}: \quad E_2 = \gamma \cdot E_0(1-\gamma)$$

$$\text{threshold energy}: \; E_{\text{th}} = \frac{E_s}{\gamma(1-\gamma)} \quad (E_s : \text{surface binding energy}) \qquad 3.5\,\text{eV} < E_s < 9\,\text{eV}$$

Physical Sputtering

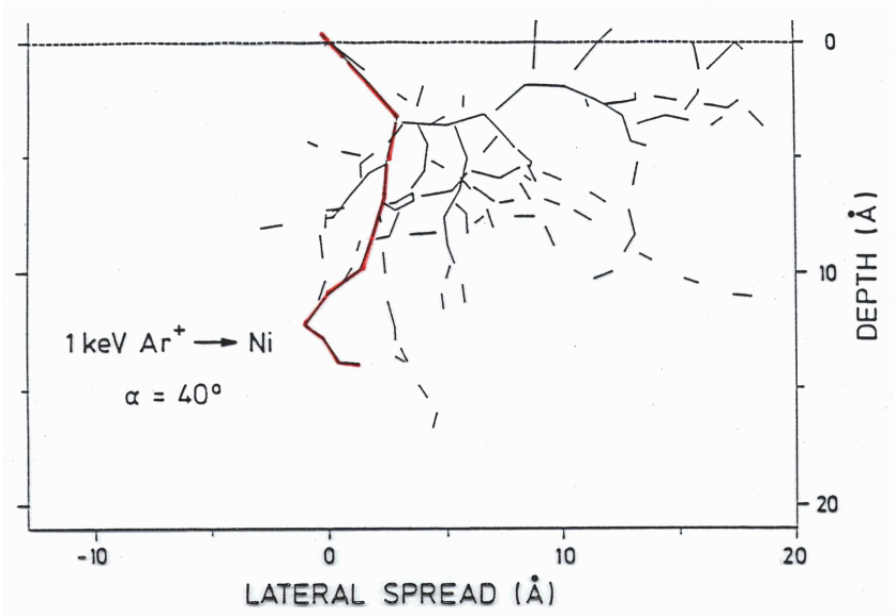
$$\text{sputter yield} \quad Y = \frac{\text{average No of sputtered particles}}{\text{incident ion}}$$

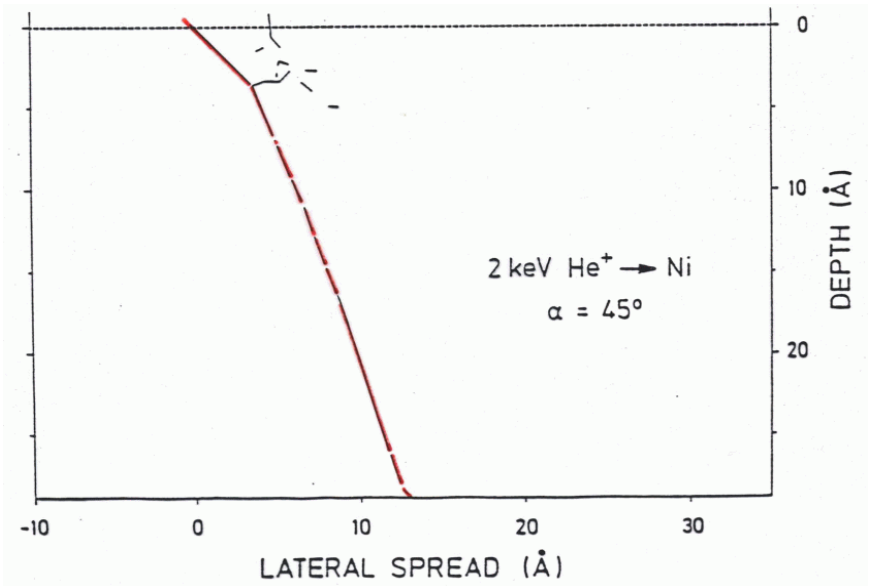


$m_1 = m_2$ (extended collison cascade) : $E_{\text{th}} = 4E_s$ (self sputtering), $3.5\,\text{eV} < E_s < 9\,\text{eV}$

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

Collision cascade





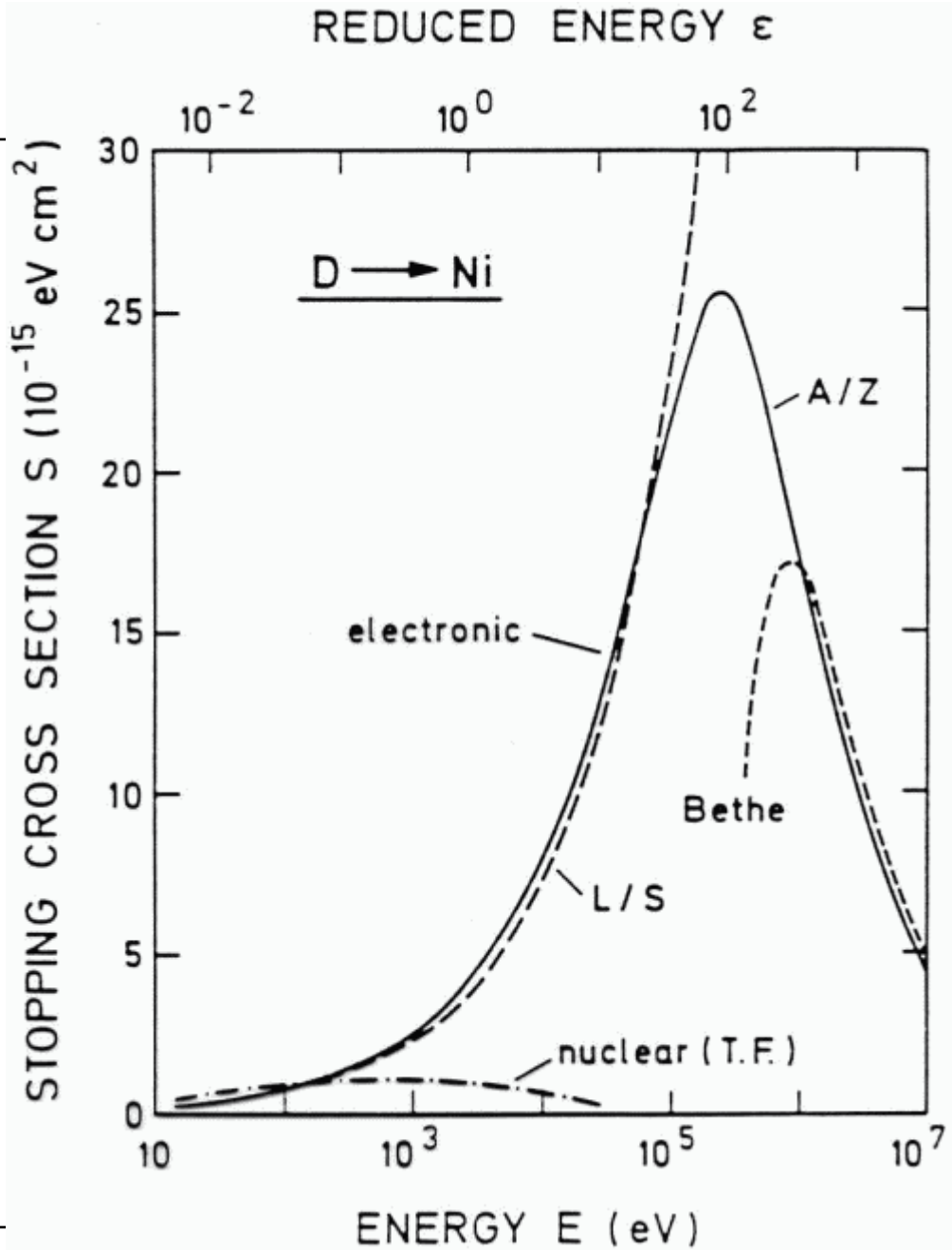
- TRIM.Sp Monte-Carlo Code

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

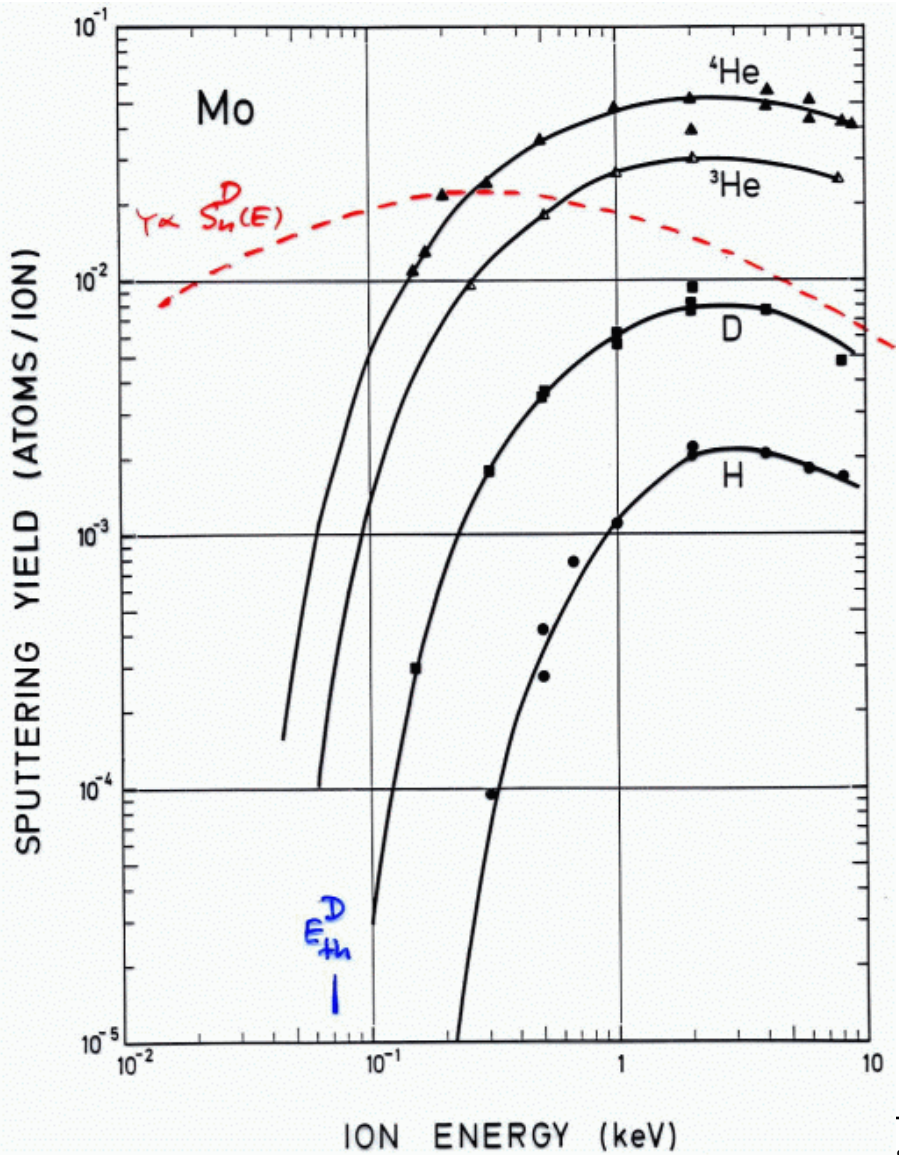
- $T = E_0 \frac{M_1 M_2}{(M_1 + M_2)^2} \cos^2 \delta$

Stopping power



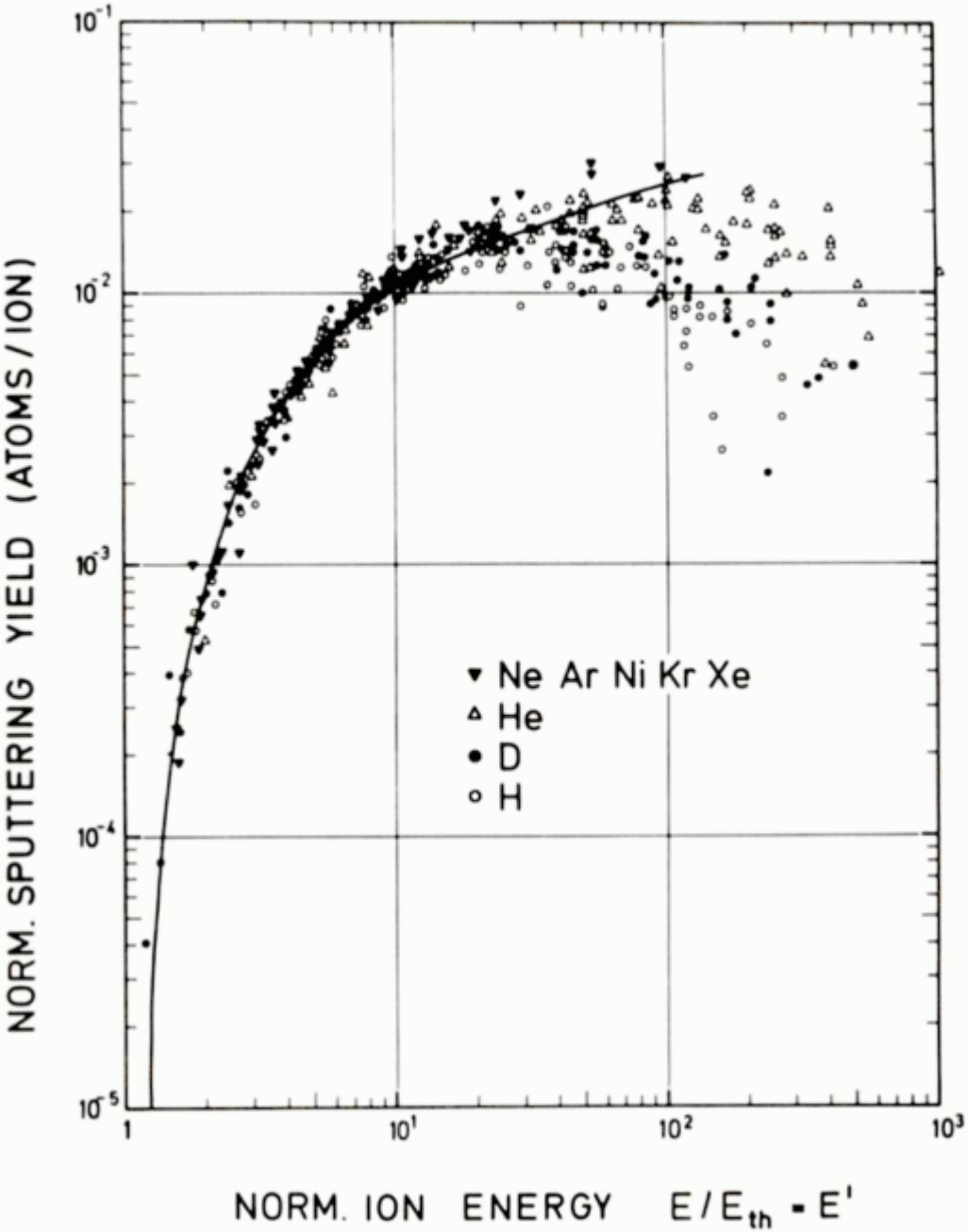
- Projectiles and recoil atoms loose energy in elastic collisions (nuclear stopping) and collisions with electrons (inelastic stopping)
- The stopping cross section is a universal function if plotted versus the reduced energy ε
- $$\varepsilon = E_0 \frac{M_2}{M_1 + M_2} \frac{a}{Z_1 Z_2 e^2} = \frac{E_0}{E_{TF}}$$
- $$S_n(\varepsilon) = \frac{0.5 \ln(1 + 1.2288\varepsilon)}{\varepsilon + 0.1728\sqrt{\varepsilon} + 0.008\varepsilon^{0.1504}}$$

Threshold regime



- Light ion sputtering in fusion application is dominated by threshold effects
- Self-sputtering due to re-deposited target atoms can be described by the isotropic collision cascade

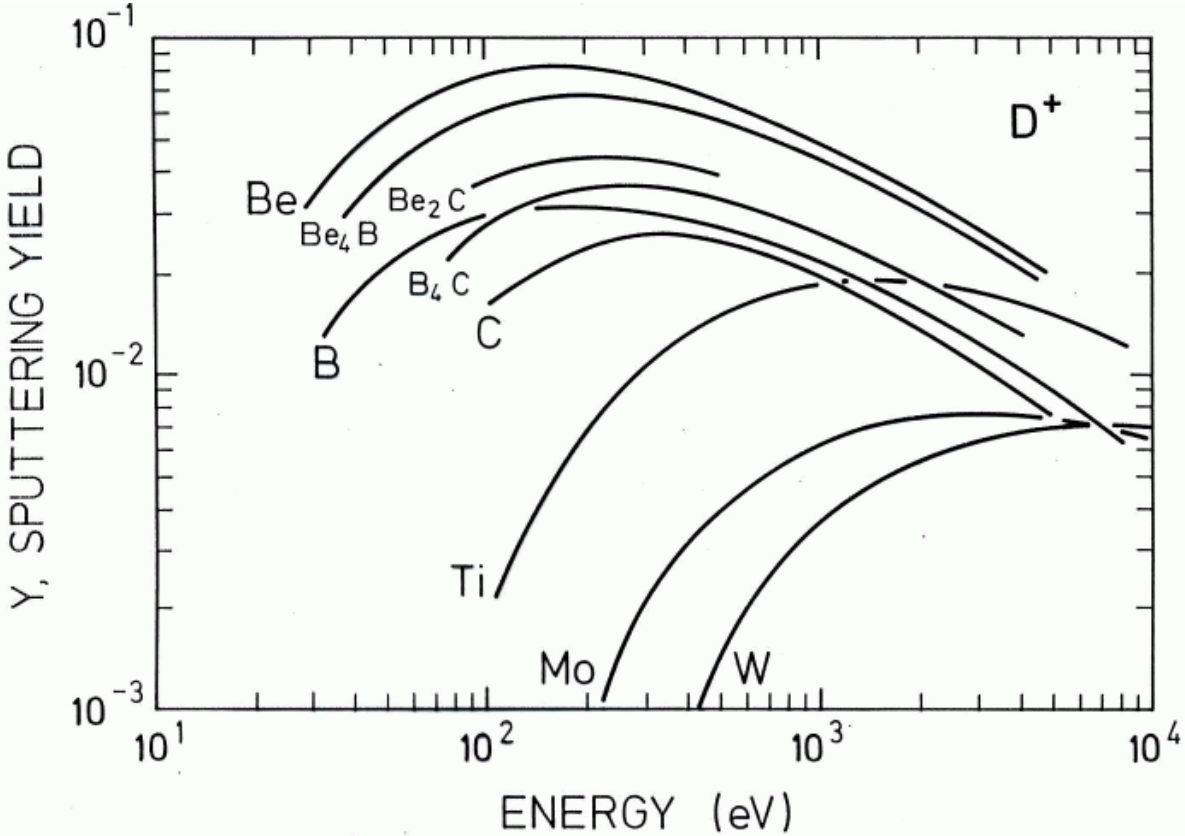
Threshold function



- 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

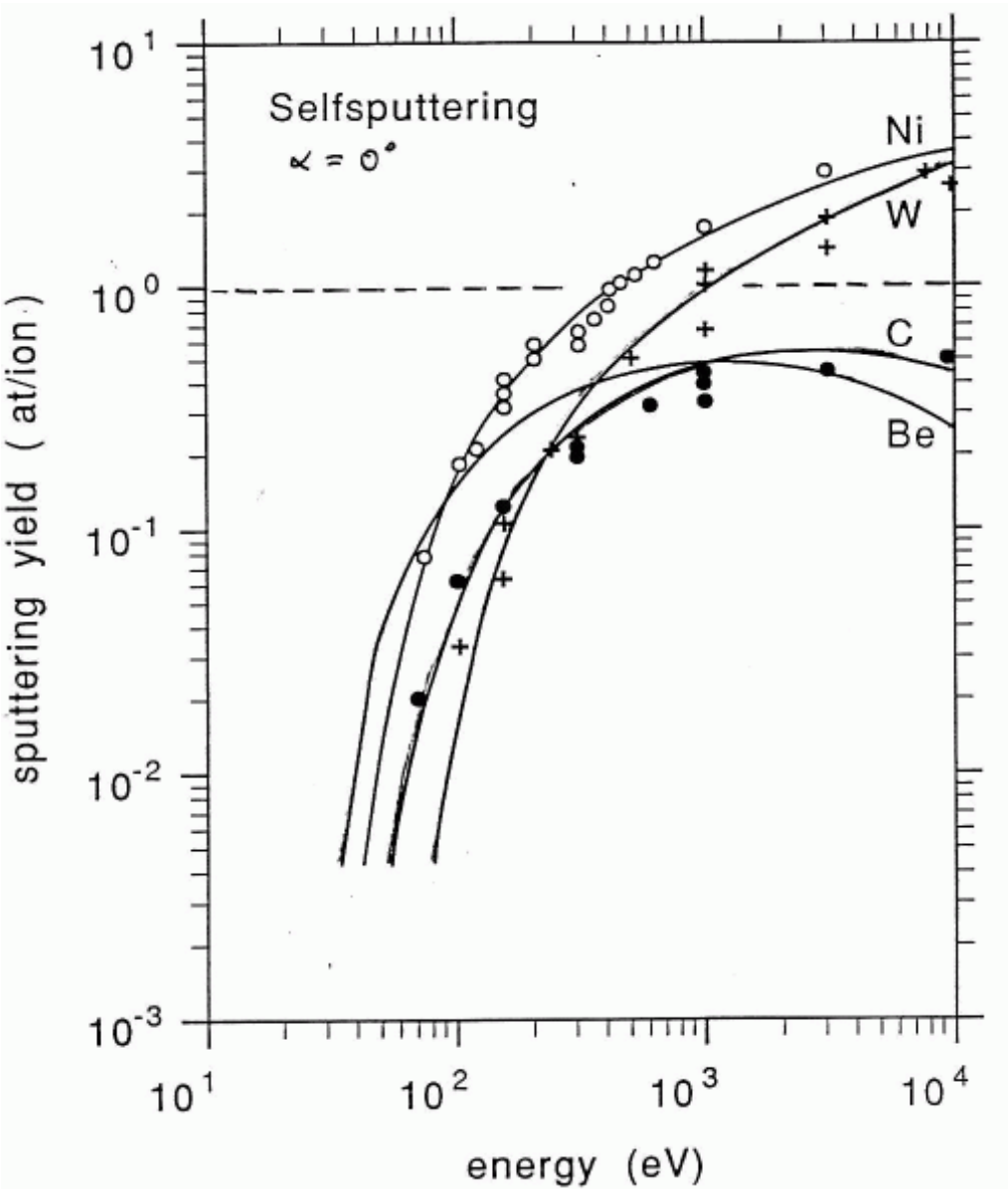
$$Y(E') = (1 - \frac{1}{E'})^{3.5}$$

Systematics for light ions



- Similar yields in isotropic cascade regime
- Strong influence of Z_2 on threshold energy E_{th}

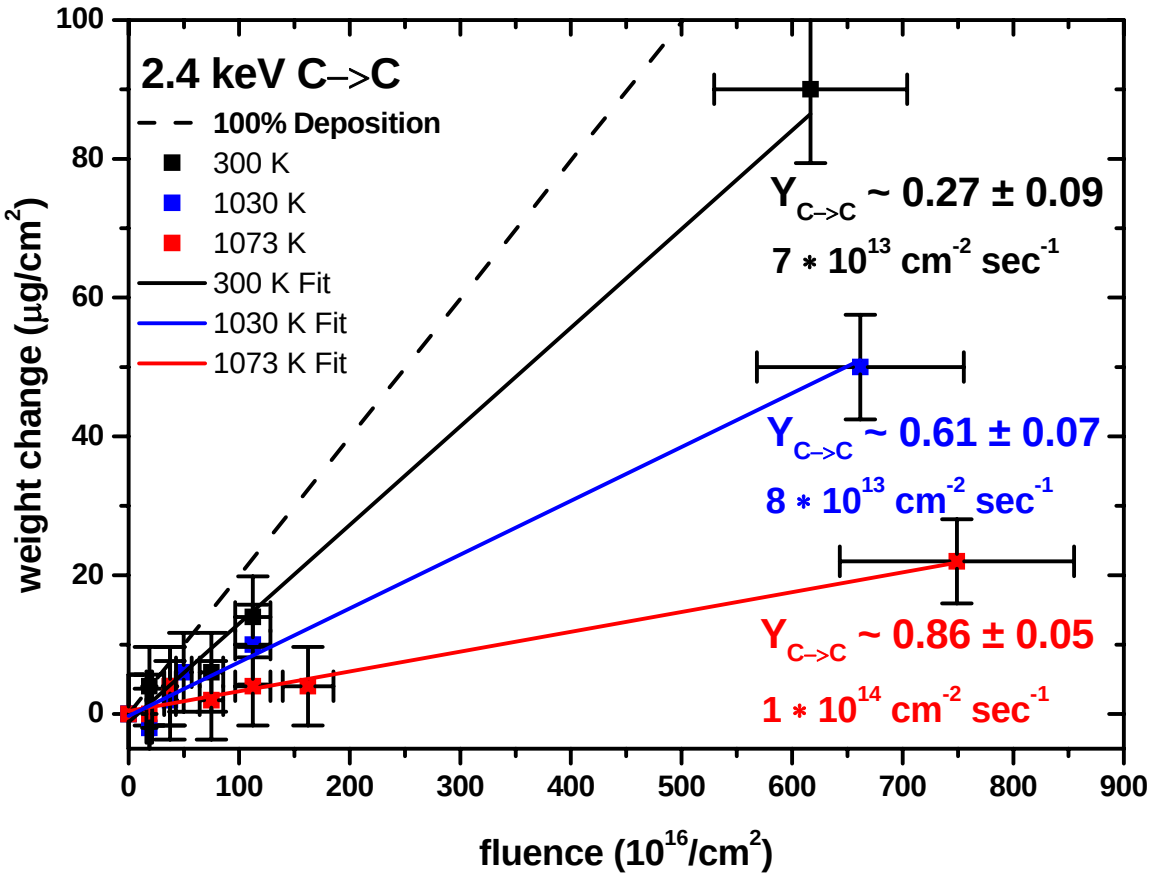
Systematics for self-sputtering



- 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 run-away impurity production may occur

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

Physical sputtering: Temperature dependence



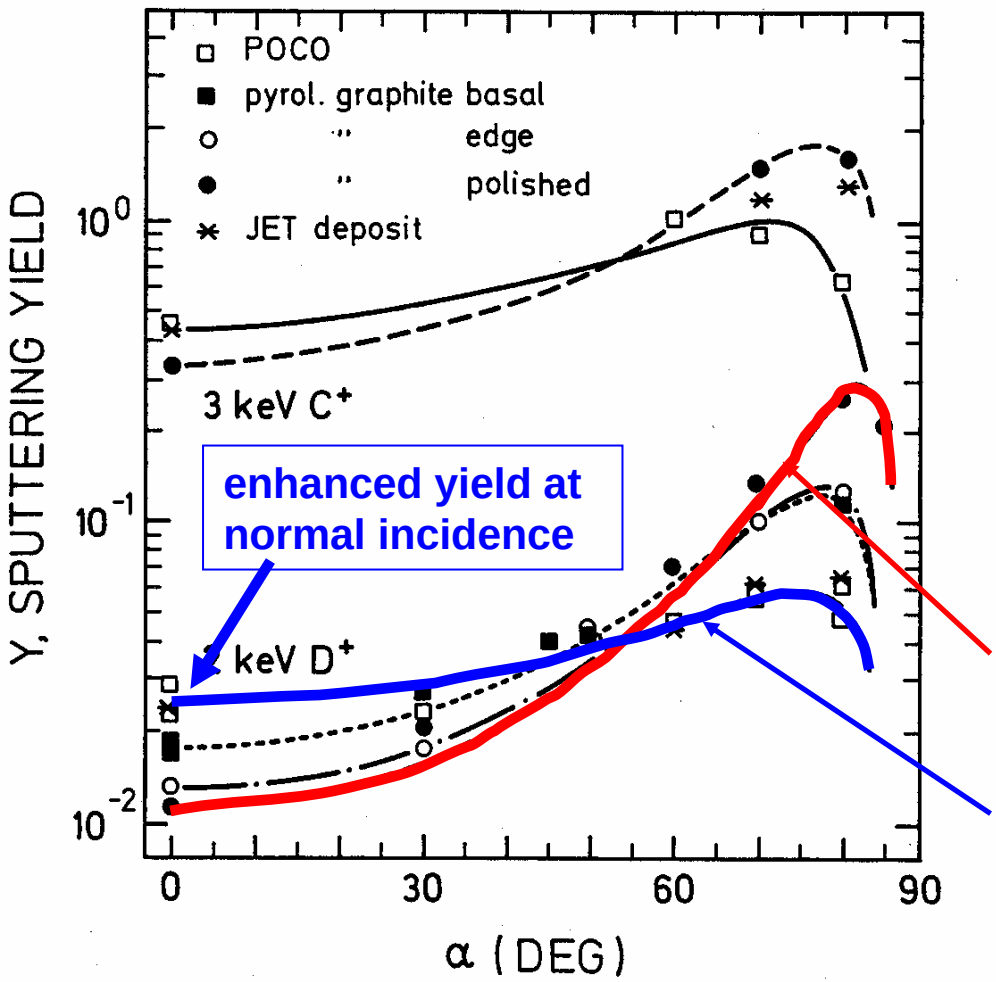
Carbon self sputtering

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



Physical sputtering yield depends on:

- angle of incidence
- substrate material
- target roughness

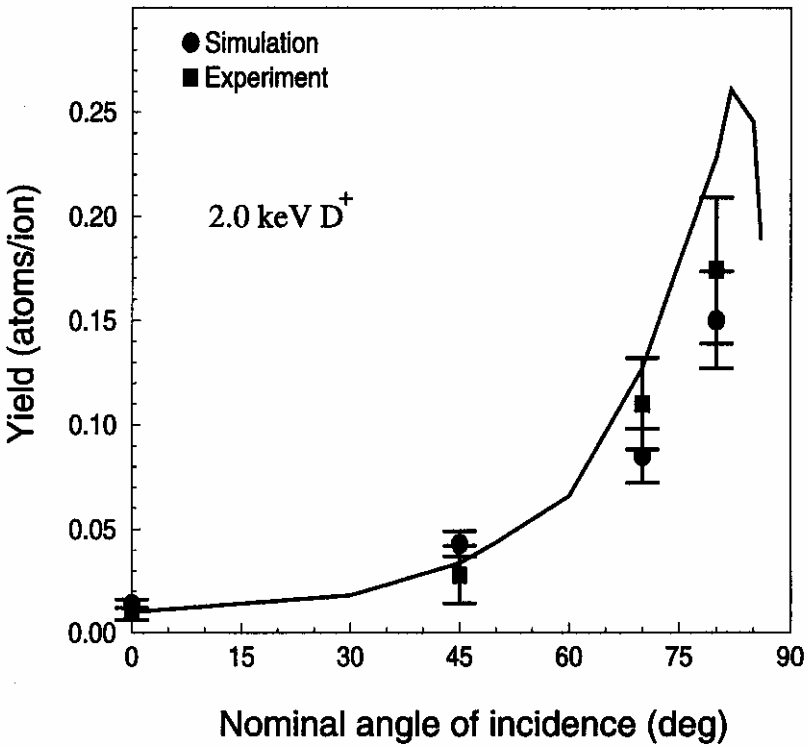
Highly-oriented, smooth graphite

Rough graphite

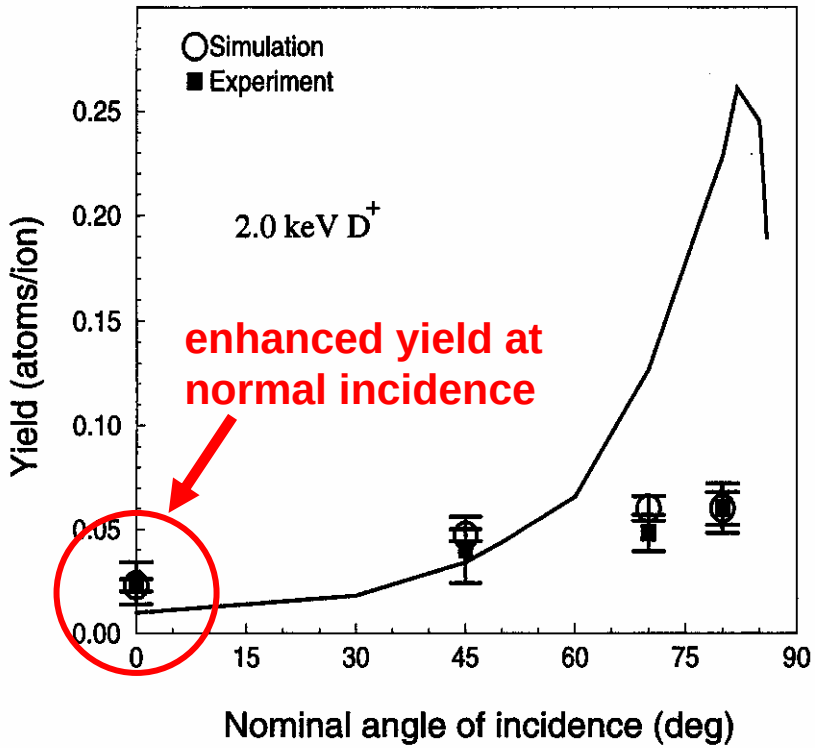
J. Roth, W. Eckstein et al., J. Nucl. Mater. ***179-181****, 34 (1991)*

Physical sputtering: Angular dependence

Highly-oriented, smooth graphite



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

Physical sputtering

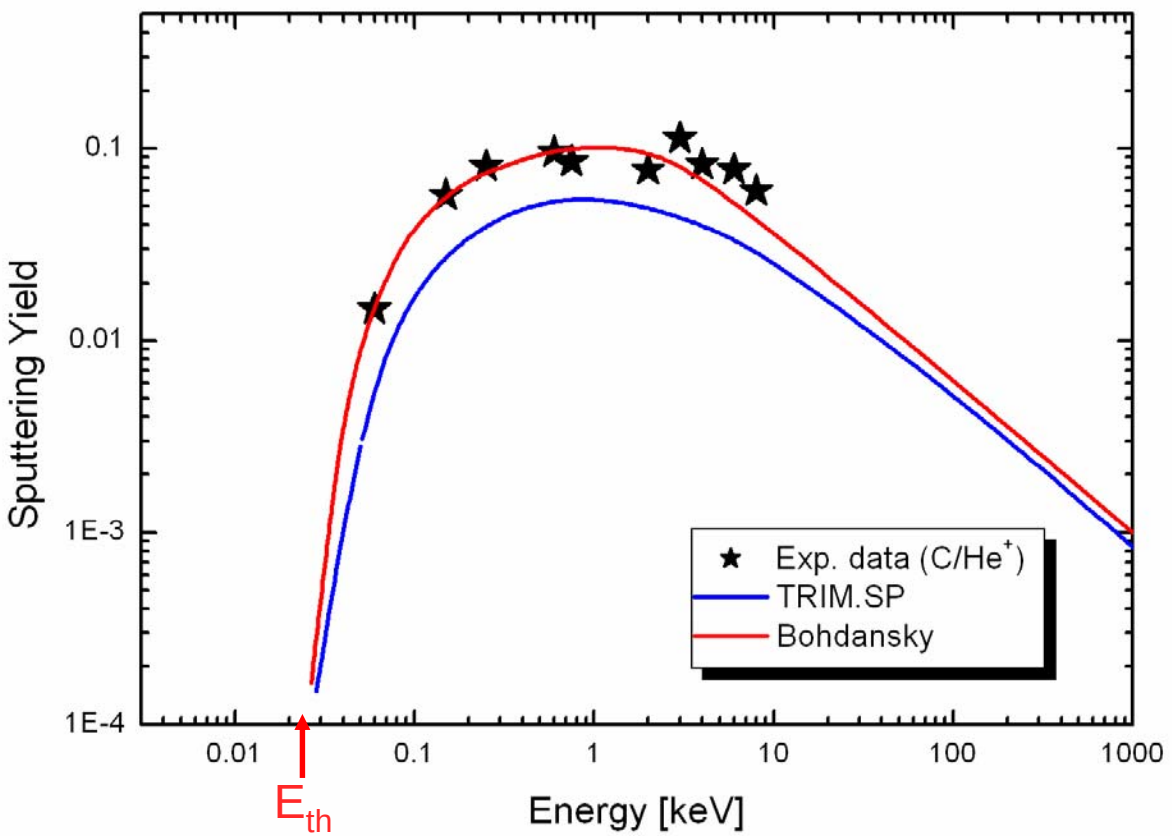
- well understood (for the most part)
- key parameter is the surface binding energy E_{SB} (= 7.4 eV for carbon)
- depends on particle energy → energy transfer:
- depends on particle mass → $T_{max} = 4\, M_1\, M_2 / (M_1 + M_2)^2$
- depends on the particle atomic number → isotope effect

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

Quantitative description of Physical Sputtering



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

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

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

$$\varepsilon = E_o \frac{M_{target}}{M_{ion}+M_{target}} . \frac{a_L}{Z_{ion}.Z_{target}}$$

$$Q = 0{,}169 \quad [atoms/ion]$$

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

*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

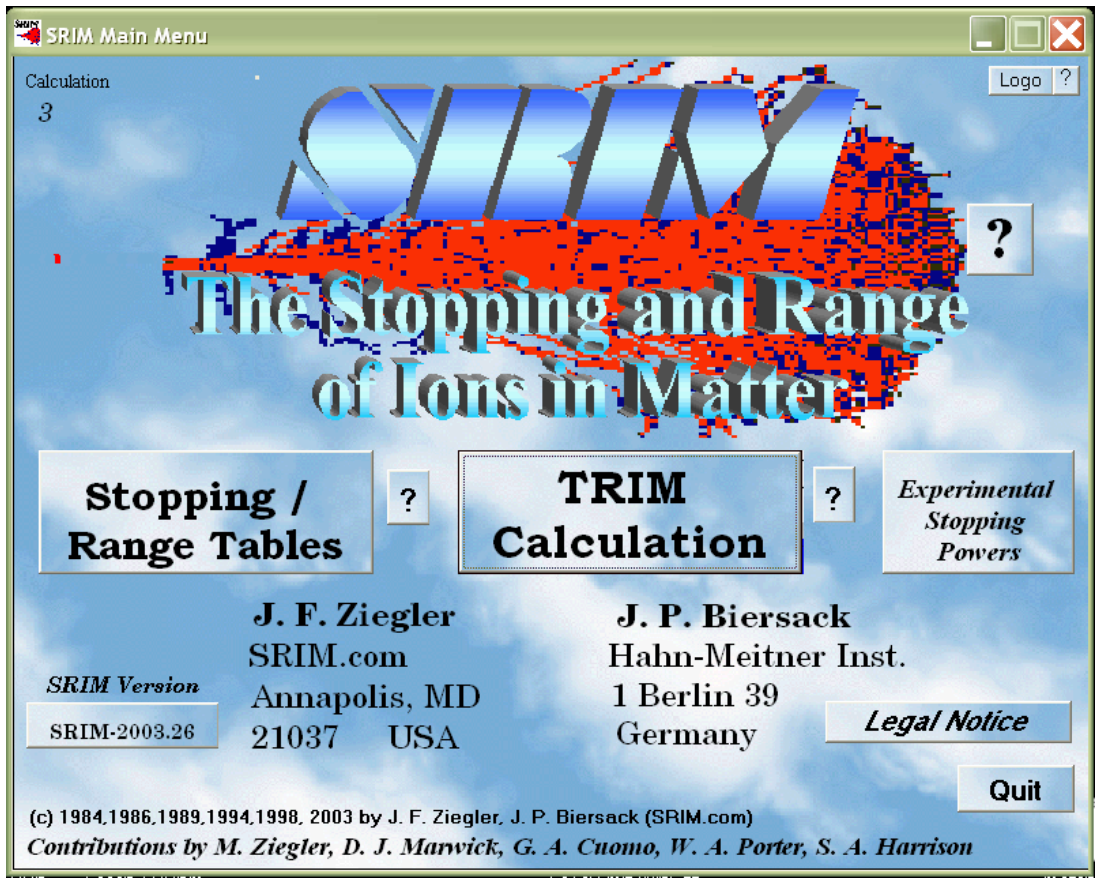
Monte Carlo Simulations based on the ***binary collision approximation***

- 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)

:
:



Physical Sputtering

some remarks on TRIM and its derivates

- are very powerful tools in describing the collision cascades for nearly every projectile on every target atom out of the elemental table

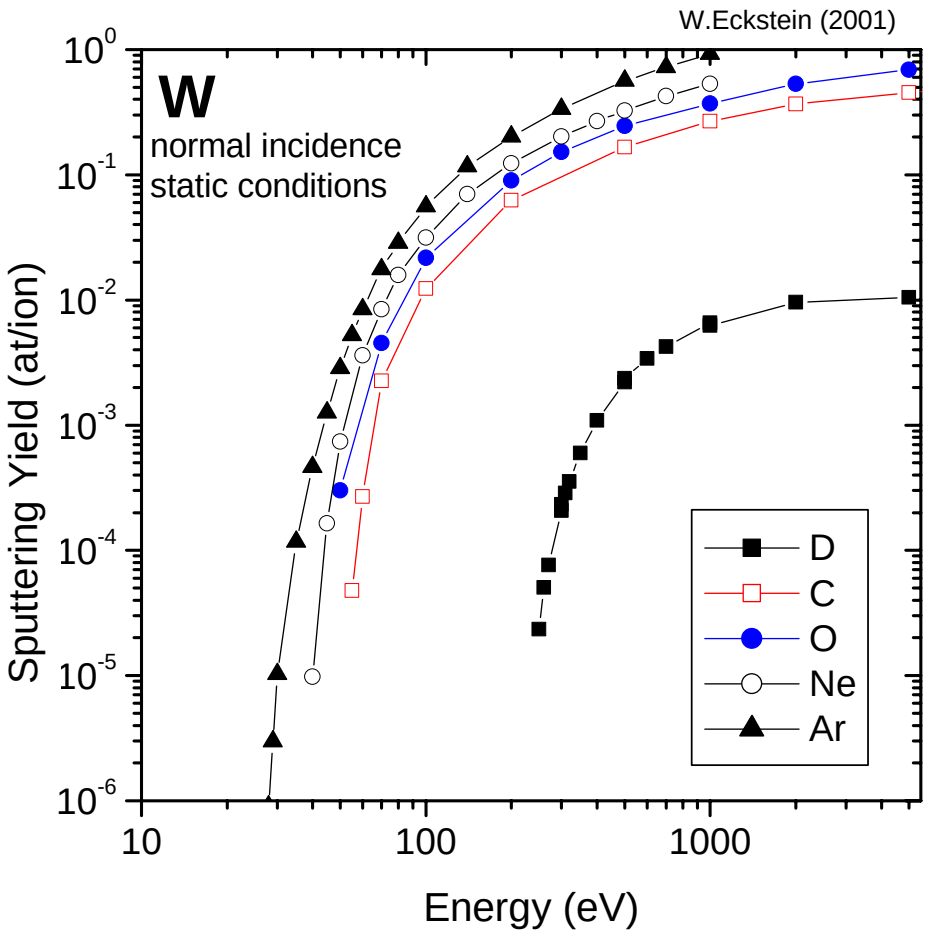
- they are not ab initio calculations but include fit parameters to describe experimental data like
  - surface binding energy
  - displacement energies

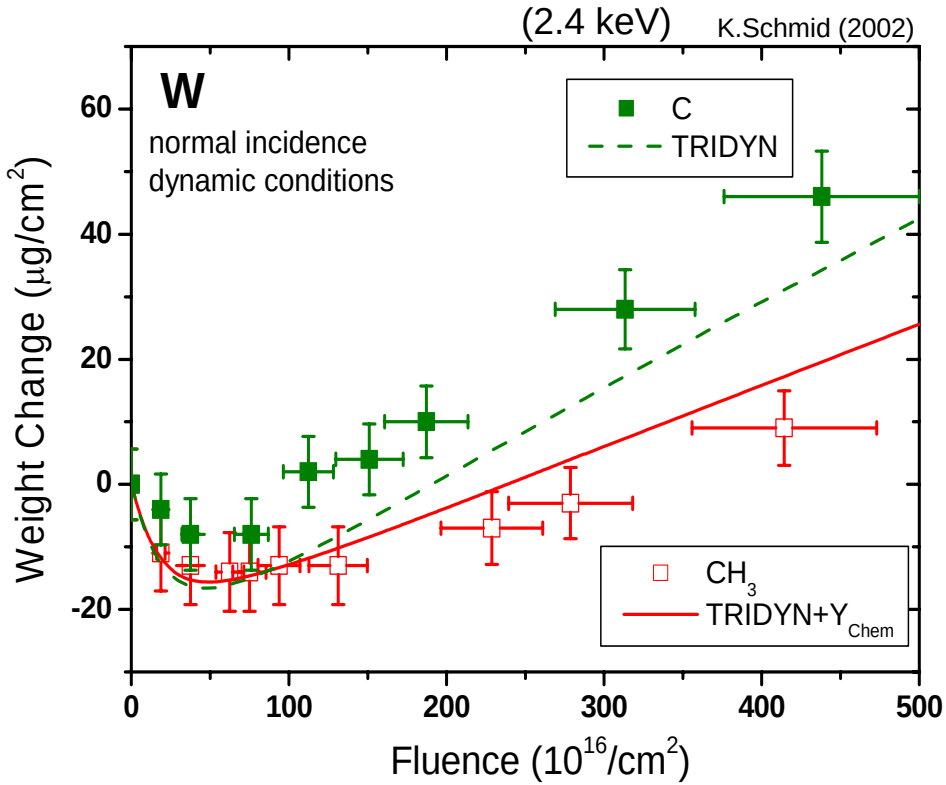
- do not include chemistry effects (bonding of H in C)

- do not include diffusion effects

- often do not change the layer composition (TRIDYN does)

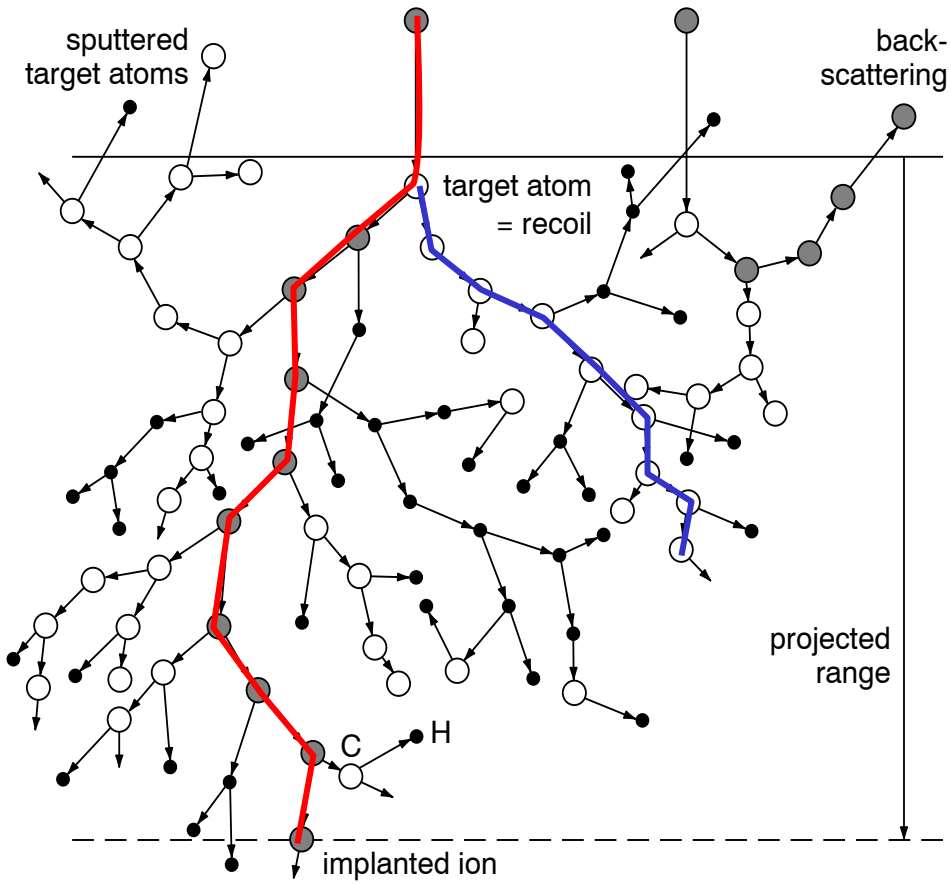
Sputtering by non-recycling ions





- TRIM.Sp for static conditions
- TRIDYN for dynamic conditions
- Data base published in
  Atomic and PMI Data for Fusion Vol. 7
  http://www-amdis.iaea.org *(AMBDAS)*

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

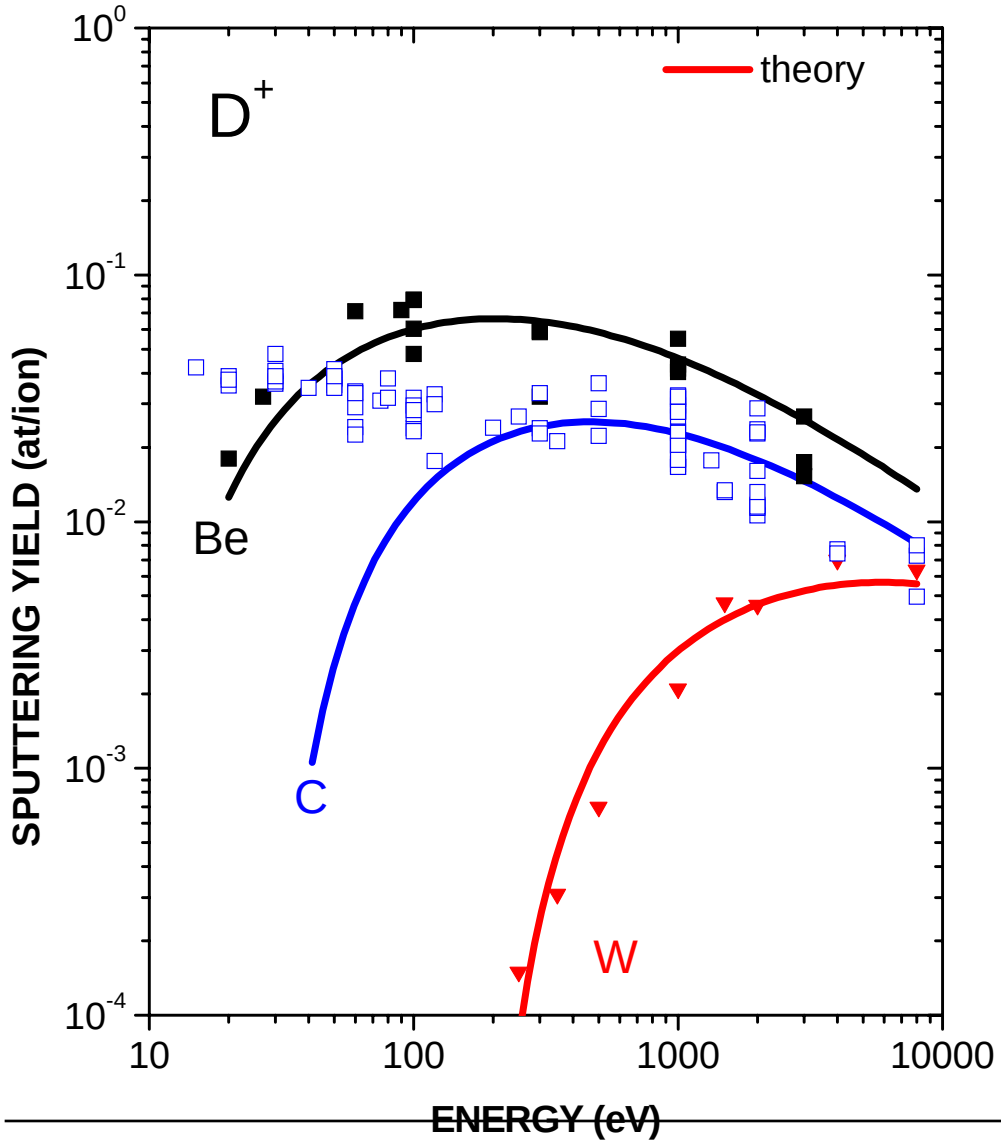
Relevant processes:

- sputtering
- implantation
- backscattering
- displacement
- activation

open questions:

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

Chemical/ physical sputtering at room temperature



- Advantage for high-Z materials
- Strong deviation for Carbon based materials
  ⇒ Chemical erosion for Carbon at low ion energies

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.

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.

Exercises

- 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 on tungsten and on carbon.
- At what energy, self-sputtering yield equals 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?