Ion, electron and photon interactions with solids: Energy deposition, sputtering and desorption

Jørgen Schou
Department of Optics and Plasma Research,
Risø National Laboratory, DK-4000 Roskilde, Denmark.
j.schou@risoe.dk

Where is Risø National Laboratory ?

Risø

Historical overview

•Sputtering discovered by Grove and Faraday	(~1850)
•Secondary electron emission discovered	(~1900)
•Charged particles identified	(~1890- 1915)
•First theoretical work on stopping	(~1915)
•Quantum theories on stopping (Bethe)	(1920 – 1930)
•Desorption models MGR	(1960)
•First comprehensive theory on sputtering	(1969)
•Fast development in studies of ion implantation and sput.	(1970-1990)
•Electronic sputtering (of water ice) discovered	(1978)

Outline

1) Introduction
2) Stopping powers (force) for ions
3) Stopping powers for electrons
4) Sputtering and desorption
5) Knock-on (collisional) sputtering
6) Electronic sputtering
7) Yields for thin films
8) Conclusion

Stopping force (stopping power)

Energy loss per length unit

$dE/dx = NS(E)$, where N is density and $S(E)$ stopping cross section.

$(dE/dx)_{total} = (dE/dx)_e + (dE/dx)_{n:}$

electronic + nuclear

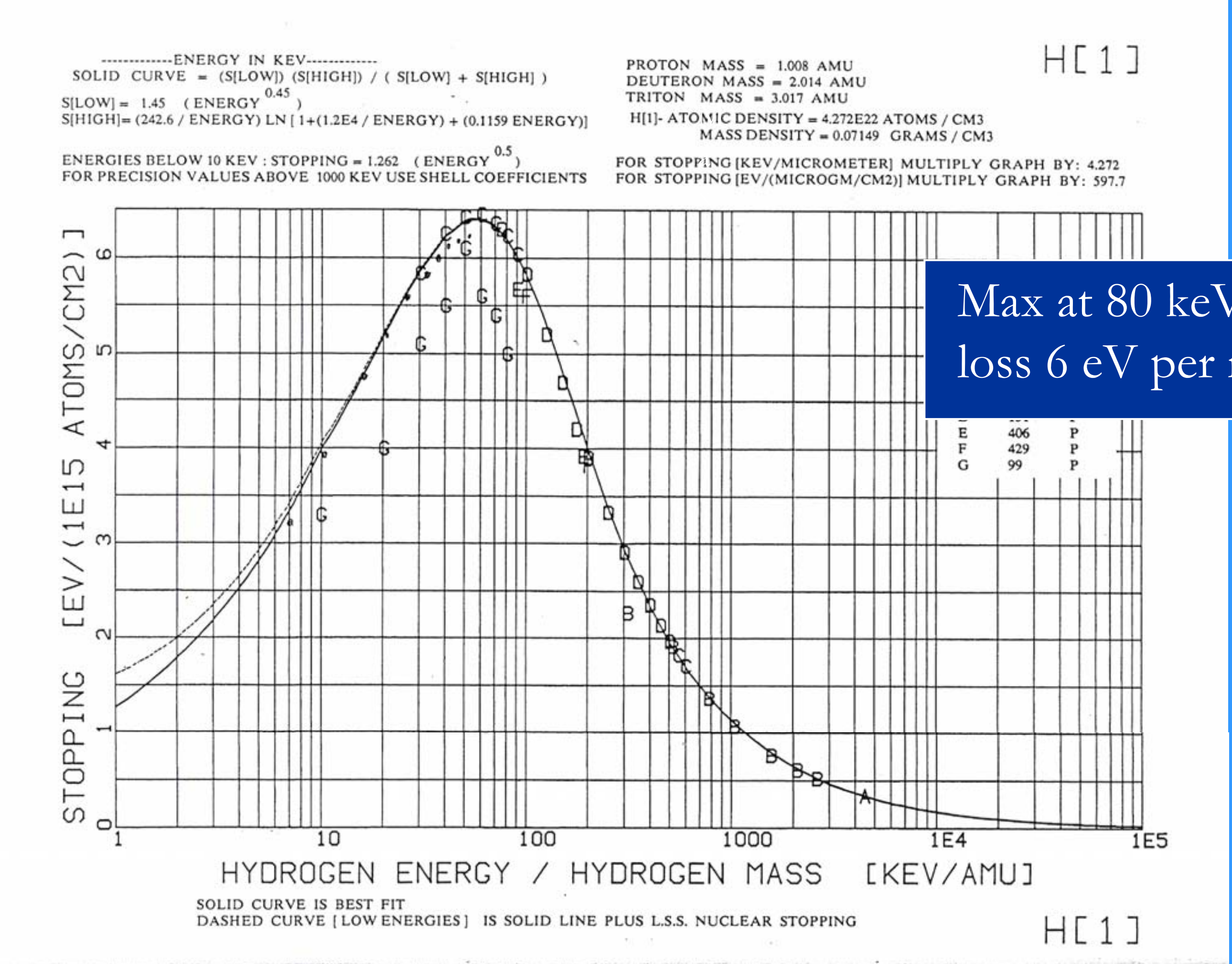
Work by Bethe, Bohr and Lindhard

See textbook: Peter Sigmund, ”Particle penetration and radiation effects” Springer, 2005

Stopping force
(Stopping power: light ion)

Low-energy side:
$dE/dx \sim v$

High-energy side:
$dE/dx \sim E^{-1}$



-------------ENERGY IN KEV-------------
SOLID CURVE = (S[LOW]) (S[HIGH]) / (S[LOW] + S[HIGH])
S[LOW] = 1.45 (ENERGY $^{0.45}$)
S[HIGH]= (242.6 / ENERGY) LN [1+(1.2E4 / ENERGY) + (0.1159 ENERGY)]

ENERGIES BELOW 10 KEV : STOPPING = 1.262 (ENERGY $^{0.5}$)
FOR PRECISION VALUES ABOVE 1000 KEV USE SHELL COEFFICIENTS

PROTON MASS = 1.008 AMU
DEUTERON MASS = 2.014 AMU
TRITON MASS = 3.017 AMU
H[1]- ATOMIC DENSITY = 4.272E22 ATOMS / CM3
MASS DENSITY = 0.07149 GRAMS / CM3

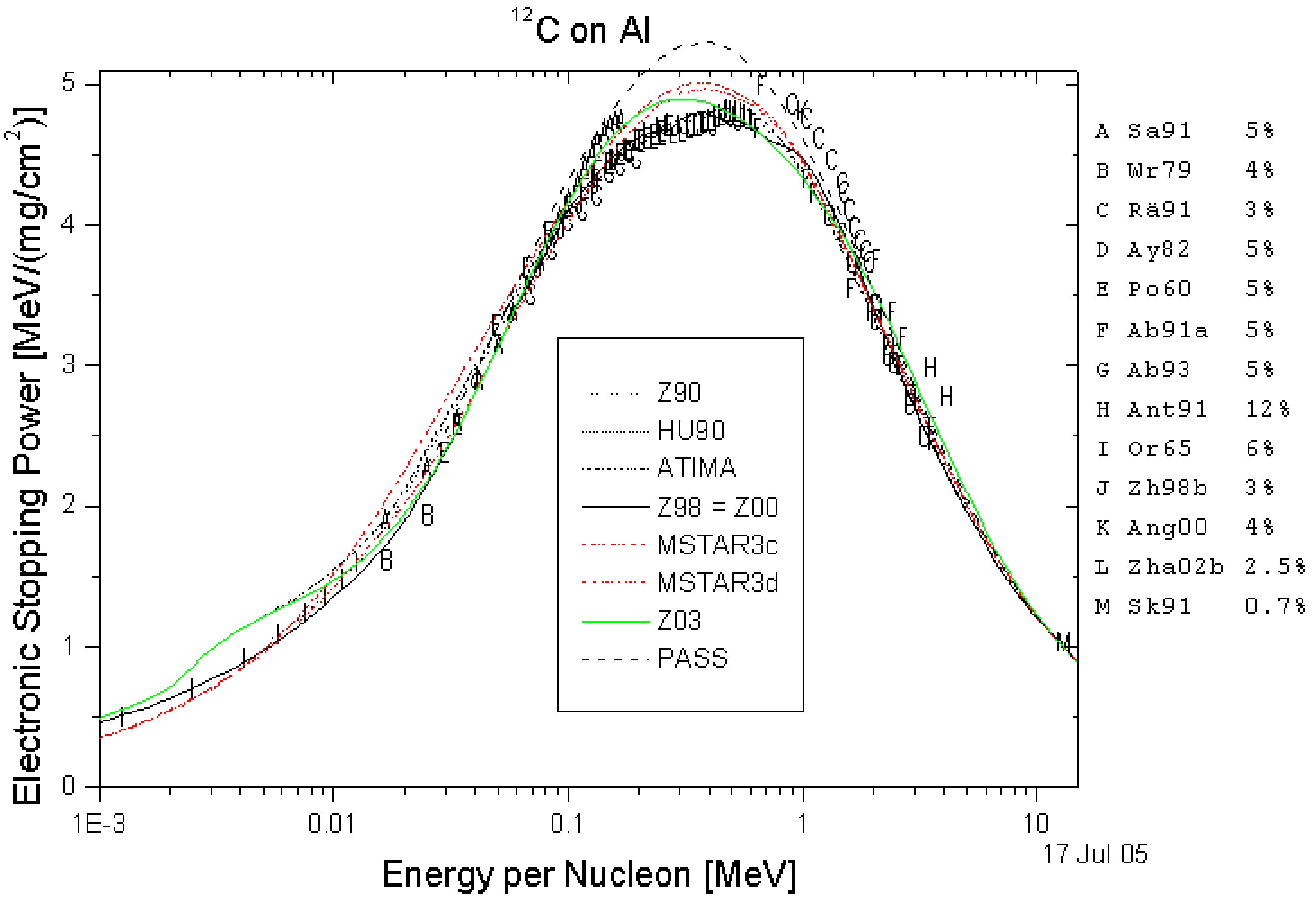
FOR STOPPING [KEV/MICROMETER] MULTIPLY GRAPH BY: 4.272
FOR STOPPING [EV/(MICROGM/CM2)] MULTIPLY GRAPH BY: 597.7

SOLID CURVE IS BEST FIT
DASHED CURVE [LOW ENERGIES] IS SOLID LINE PLUS L.S.S. NUCLEAR STOPPING

Max at 80 keV:
loss 6 eV per monolayer

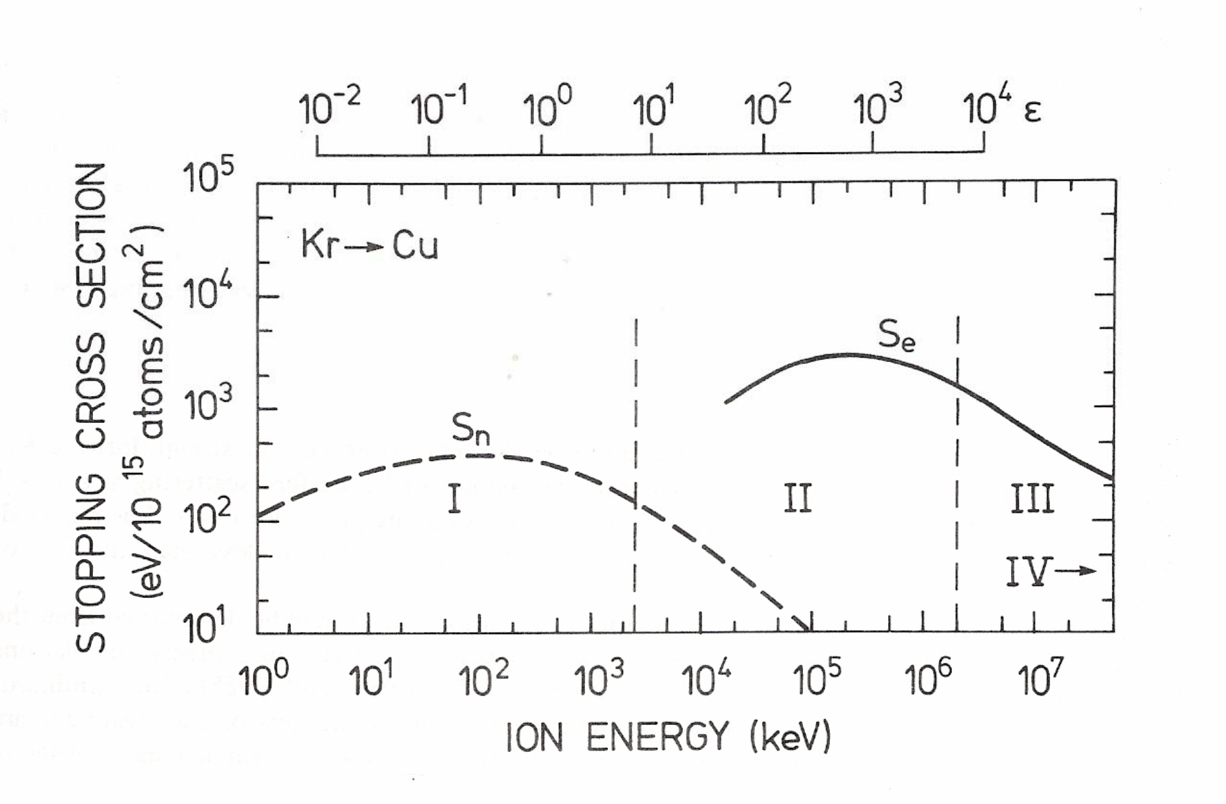
From H. H. Andersen and J. F. Ziegler, ”Hydrogen Stopping Power and Ranges in all Elements”, Pergamon, New York (1977)

Stopping force



www. exphys.uni-linz.ac.at/stopping/

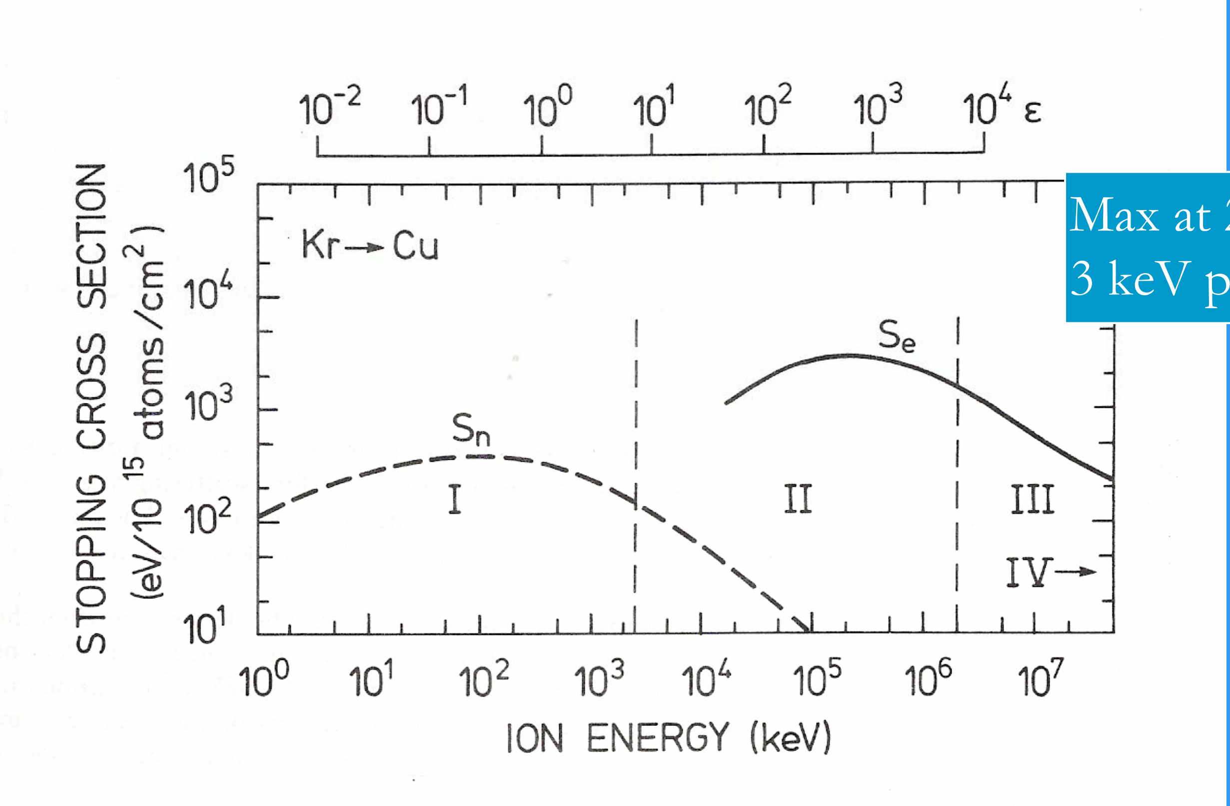
Stopping force (Stopping power)



S_n :nuclear stopping cross section S_e electronic stopping cross section

From J. F. Ziegler, ”Handbook of Stopping Cross Section for Energetic Ions in All Elements”, Pergamon, New York (1980).

Stopping force (Stopping power)

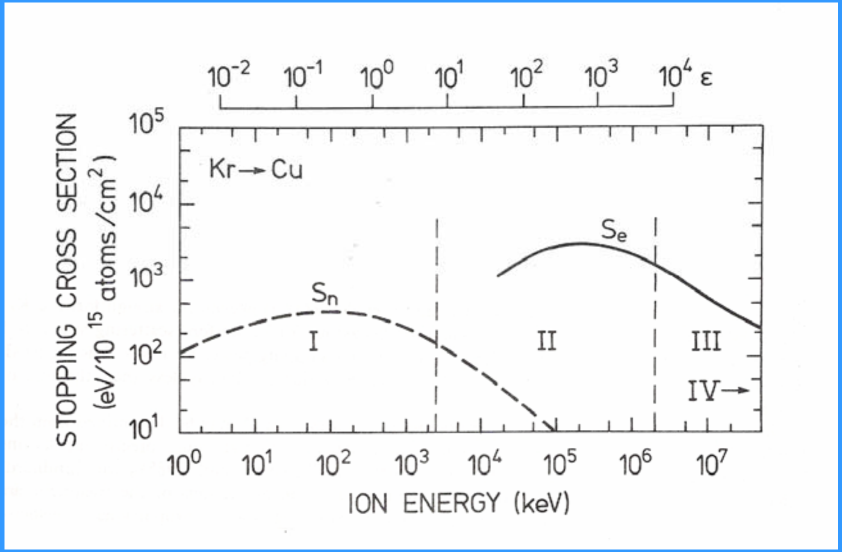


Max at 200 MeV Kr
3 keV per ”monolayer”

S_n :nuclear stopping cross section S_e electronic stopping cross section

From J. F. Ziegler, ”Handbook of Stopping Cross Section for Energetic Ions in All Elements”, Pergamon, New York (1980).

Electronic stopping force (Stopping power) $(dE/dx)_e$



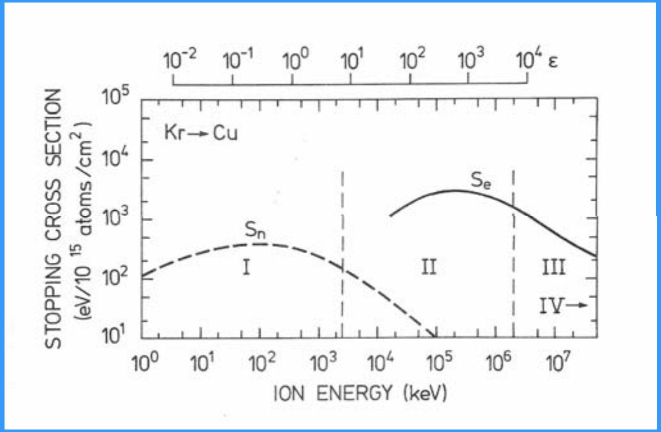
$dE/dx = NS_e$

Bohr's criterion for a classical treatment: $\varkappa = 2Z_1Z_2e^2v_B\ /(\hbar v) > 1$

Quantum treatment : $\varkappa < 1.$

Bethe treatment for light primary ions, electrons
Bohr treatment for heavy ions

Electronic stopping force (Stopping power) $(dE/dx)_e$



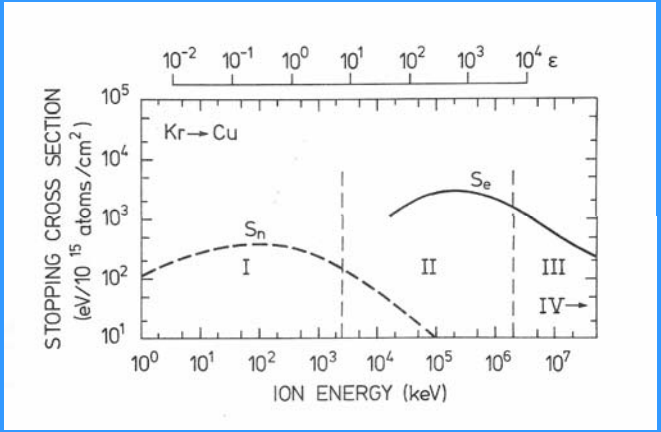
$dE/dx = NS_e$

Bohr's formula for heavy projectiles: $S_e = (4\pi Z_1{}^2 Z_2 e^2/mv^2)\ \ln(\ 1.123mv^3/|Z_1e^2|\ \omega_0)$

Bethe's formula : $S_e = (4\pi Z_1{}^2 Z_2 e^2/mv^2)\ \ln(2mv^2/I)$

Quantum treatment for light projectiles

Nuclear stopping force (Stopping power) $(dE/dx)_n$



$$(dE/dx)_n = NS_n$$

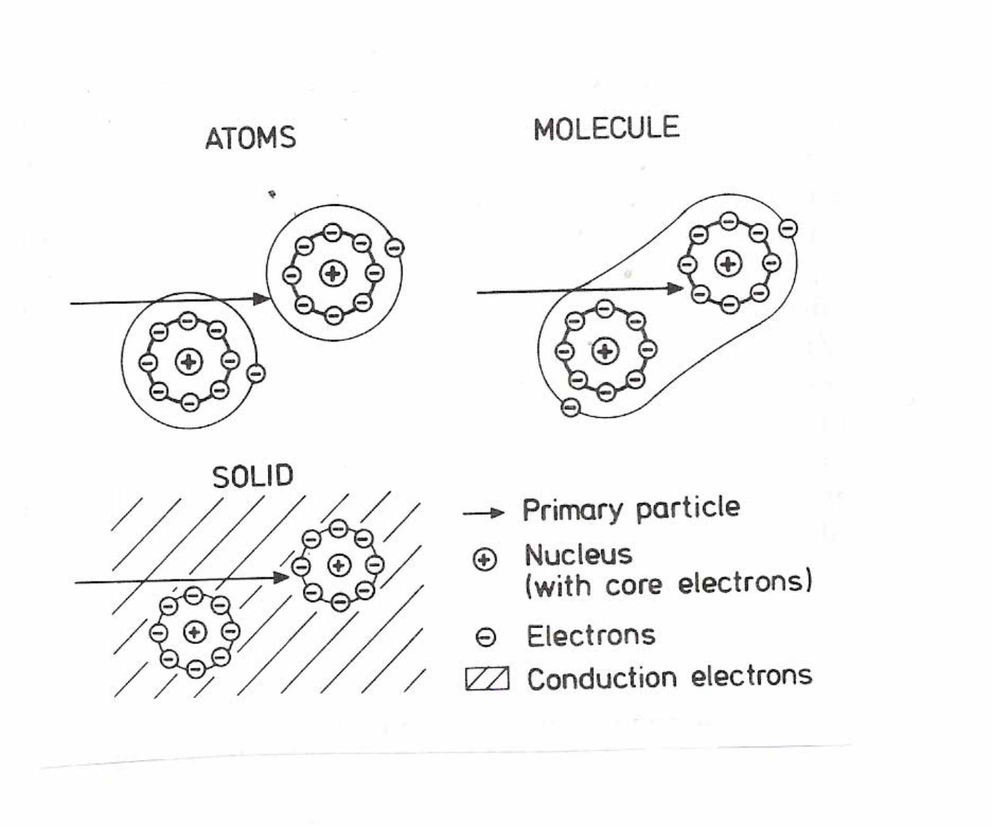
Can be described by Lindhard’s reduced nuclear stopping force : $s_n(\varepsilon)$:
Universal function for all beam-target combinations.

$$S_n(E) = \pi a_L{}^2 \gamma s_n(\varepsilon)/(\varepsilon/E)$$

$$\gamma = 4M_1M_2/(M_1 + M_2)^2$$

Lindhard et al. , Mat. Fys. Medd. Vid. Selsk. (1963).

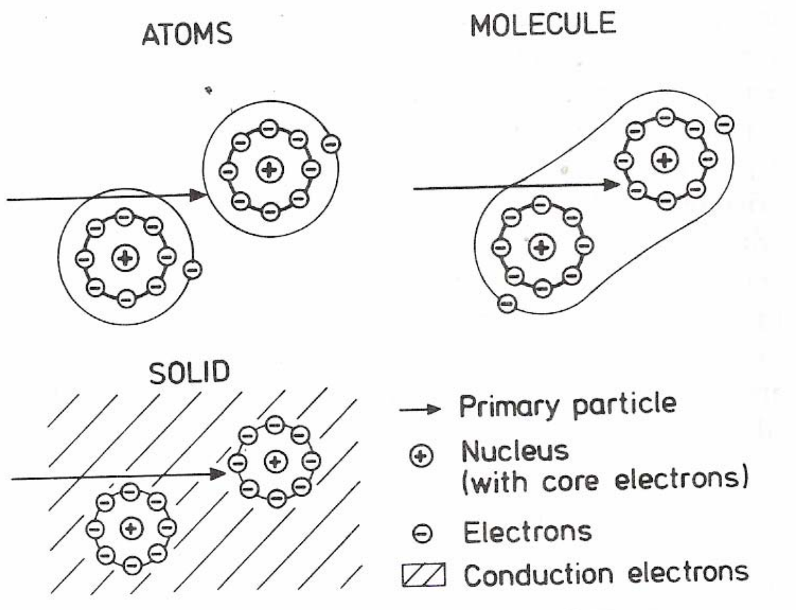
Energy loss in diff. systems (ions)



Bethe's formula : $Se = (4\pi Z12Z2e2/mv2)\ ln(2mv2/I)$
$\ln I = f_{core}I_{core} + (1-f_{core})I_{val}$

J. R. Sabin and J. Oddershede, Nucl. Instr. Meth. B 27, 280 (1987)

Energy loss in diff. systems (ions)



Only small deviations of the stopping (<10%) for changes
in solid/vapor phase and
in chemical bonds

Energy loss: Refinements.

1. Relativistic effects (high velocities)
2. Inner-shell effects (medium velocities)
3. Charge state effects (low velocities)
4. Molecular and cluster beam (more than one beam-particle)

Particles without charge exchange: antiprotons

S. P. Møller, A. Csete, T. Ichioka, H. Knudsen, U. I. Uggerhøj and H.H. Andersen, Phys. Rev. Lett. **93**, 042502 (2004)

Obtained at the Antiproton Decelerator (AD) at CERN

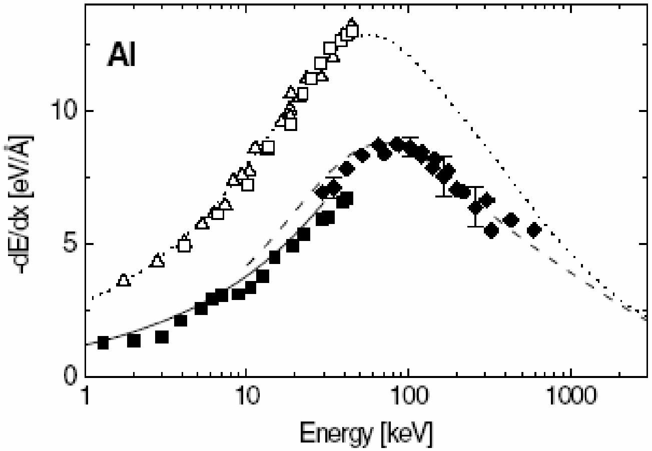
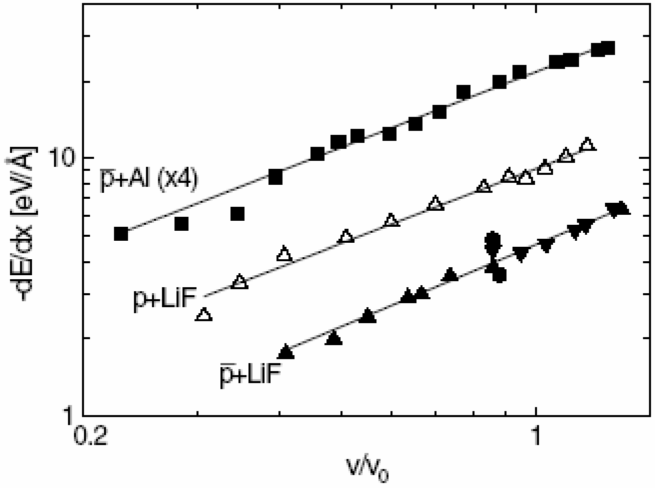
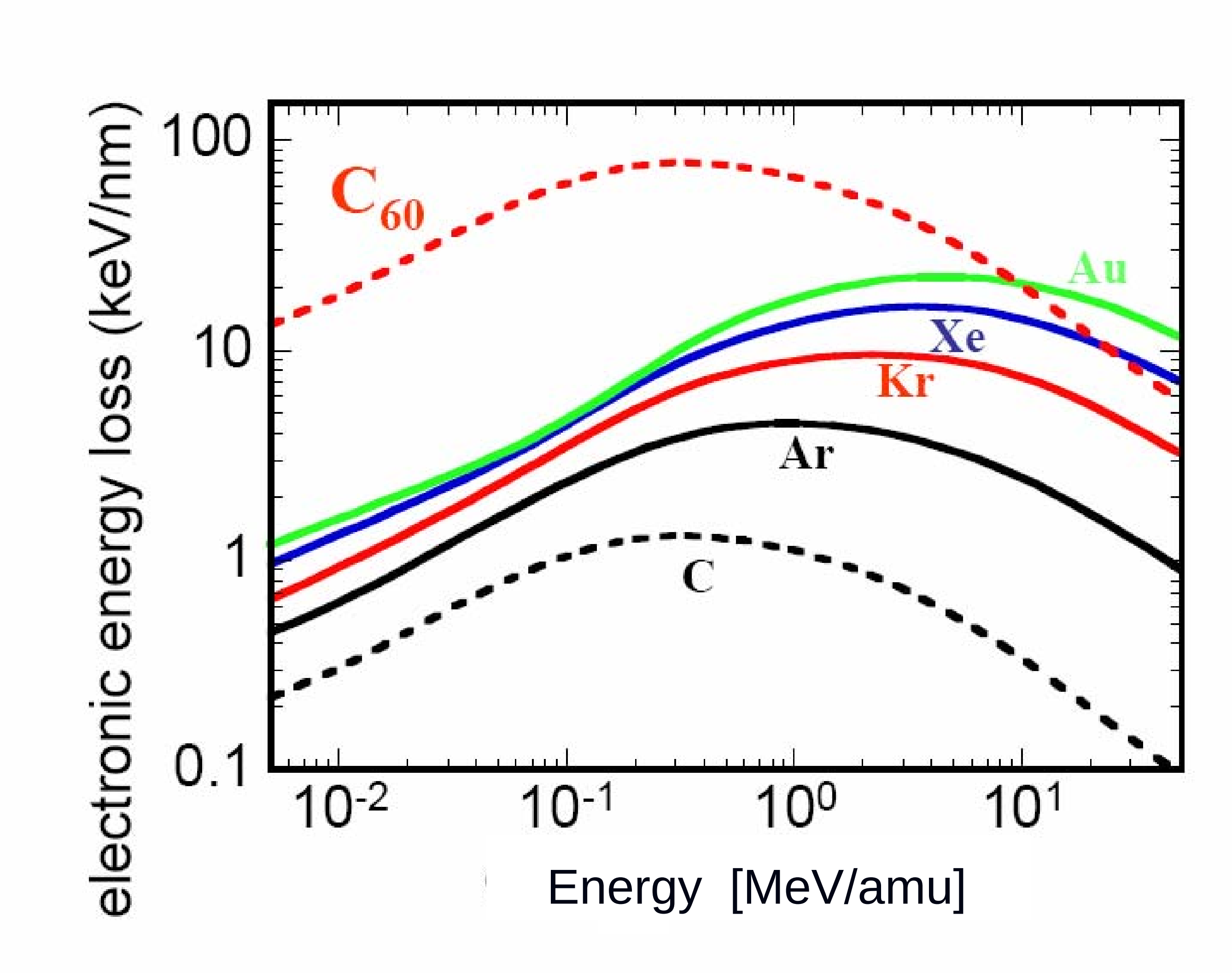


FIG. 5. Measured antiproton (■) and proton (△, □) stopping powers of Al (this work). The data ◆ are from [6]. See the text for an explanation of the curves.



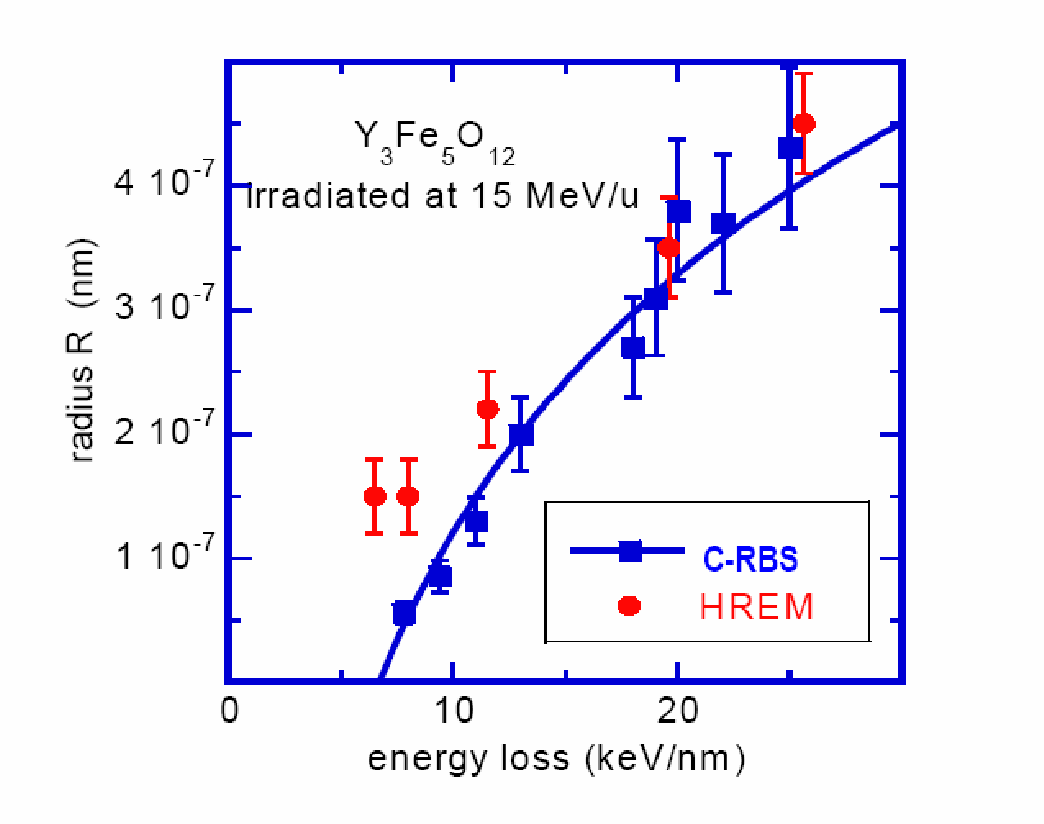
The Barkas-Andersen effect can be measured accurately with antiprotons

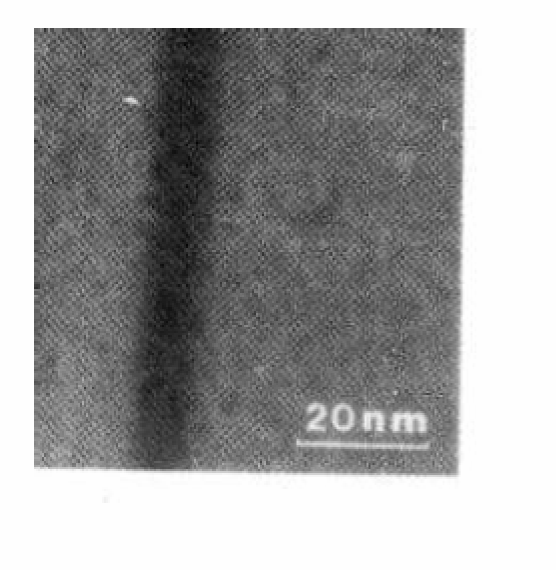
Energy loss in a-SiO_2 (ions)



From M. Toulemonde, Ion06 (unpublished).

Track structure

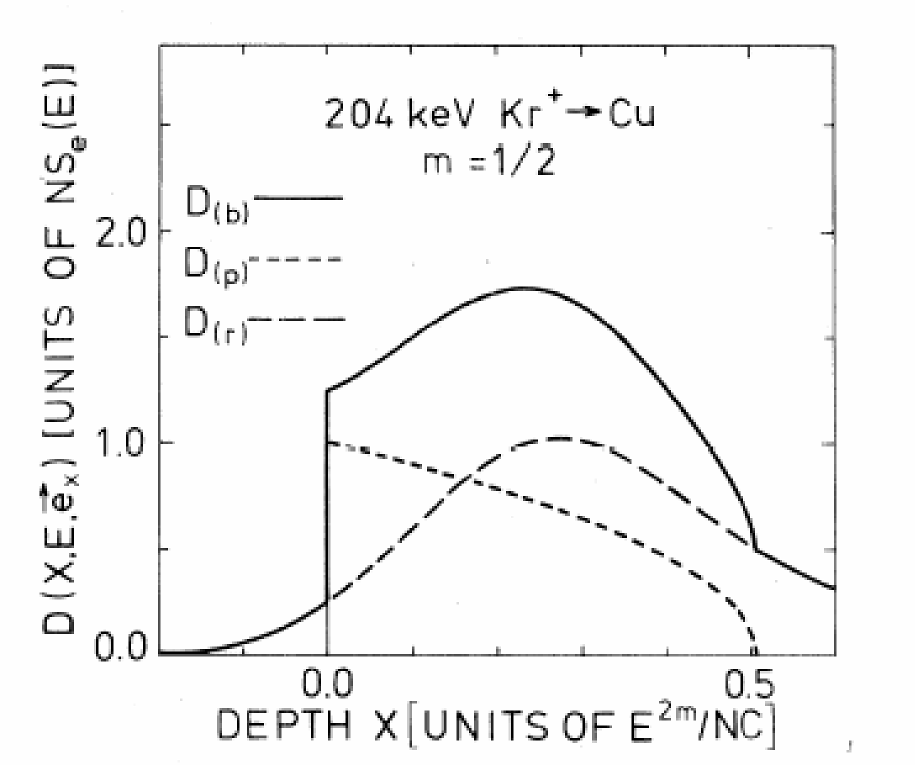




Houpert et al.

Nucl. Instr. Meth B32 (1988) 393

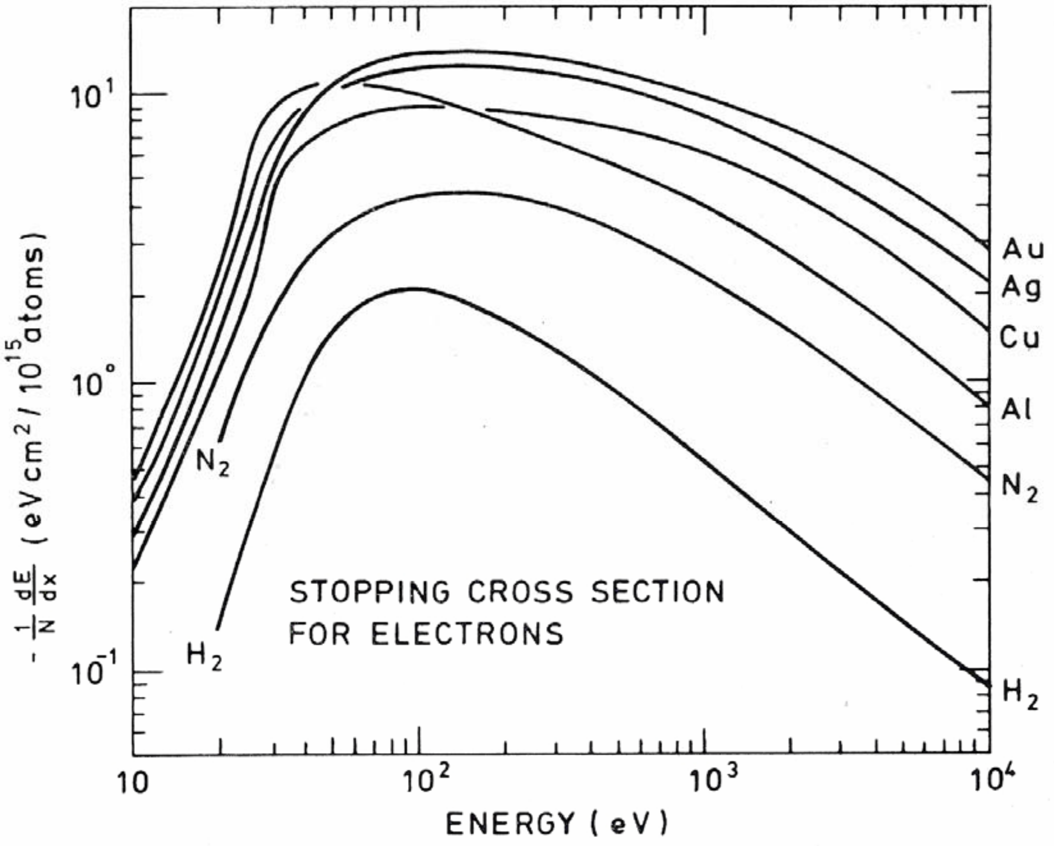
Energy deposition by ions: ”electronic energy”



Units of ”Kr range”

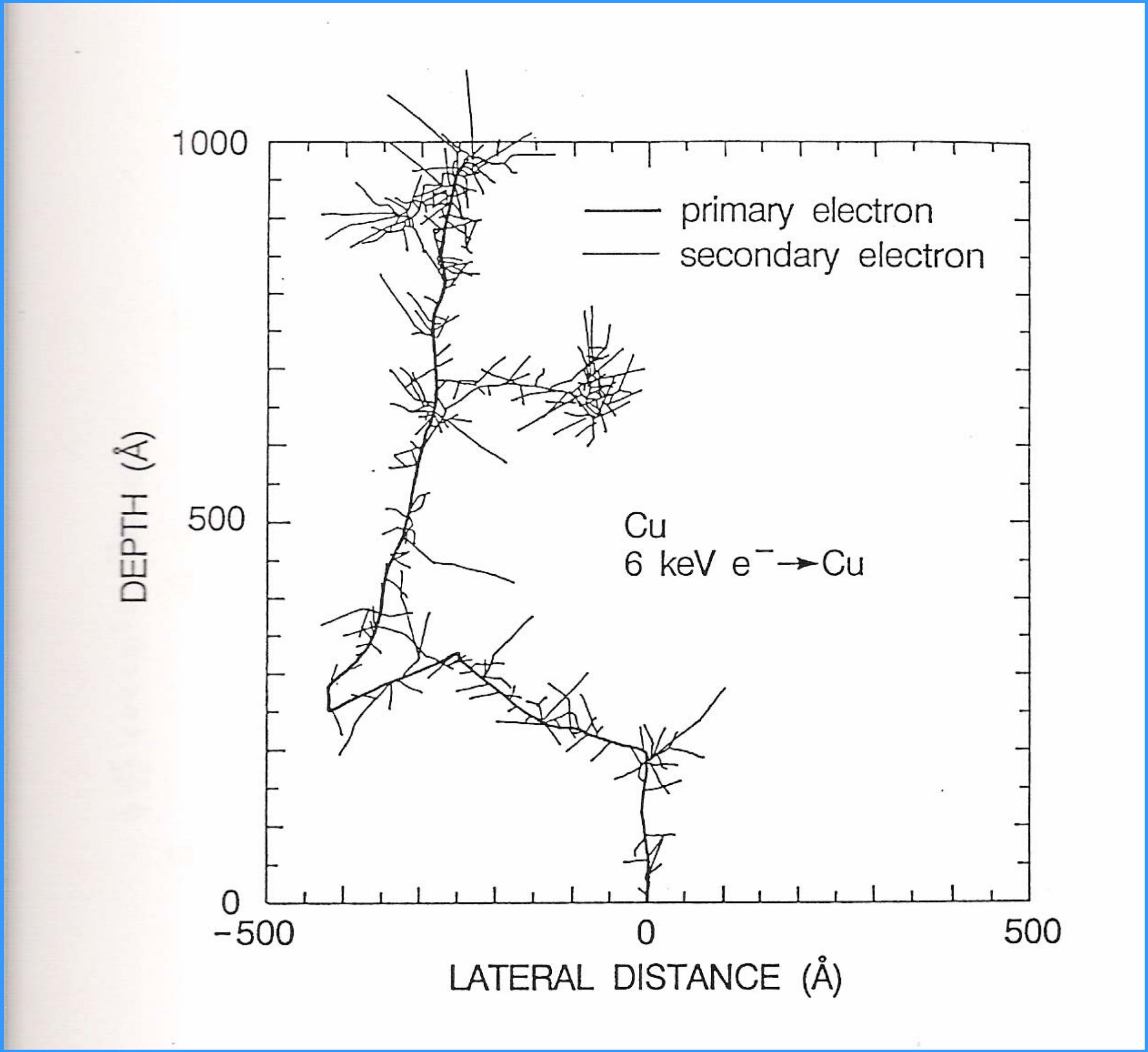
From J. Schou, Phys. Rev. B **22**, 2142 (1980)

Electron stopping force dE/dx (electrons)



Modified from J. Schou, Scan. Micr. **2**, 607 (1988)

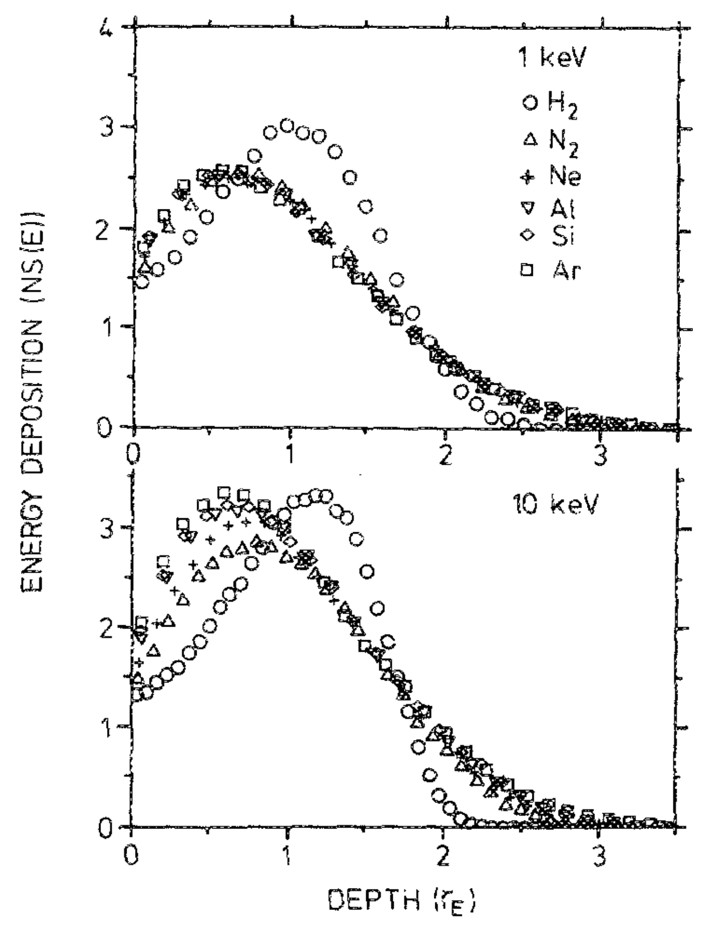
Electron trajectories



Strong scattering of electrons

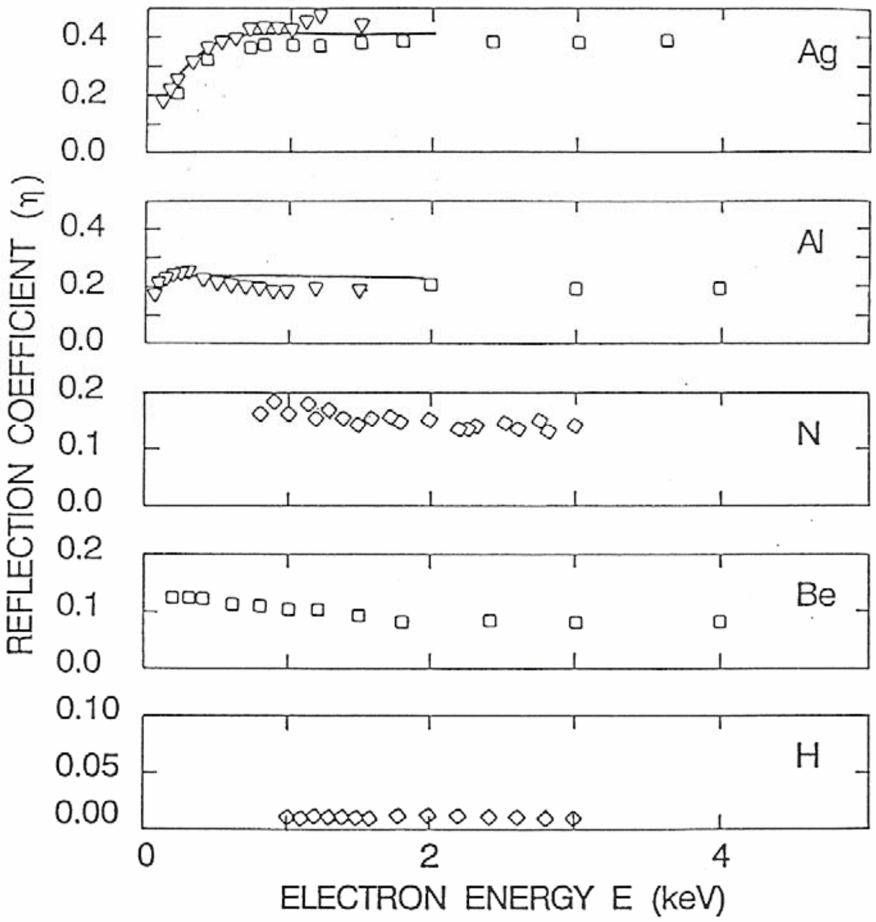
Deposited energy: electrons

From S. Valkealahti, J. Schou and R. M. Nieminen, J. Appl. Phys. **65**, 2258 (1989)



Strong scattering of electrons in solids
for energies below 10 keV

Electron backscattering



Risø National Laboratory, OFD

Summary: particle slowing down

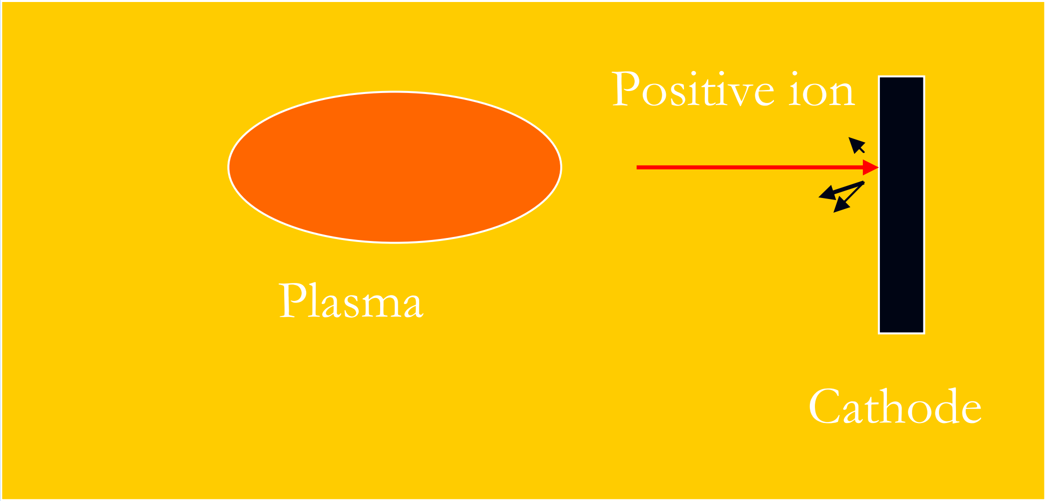
Electrons: Strong scattering below 10 keV
Stopping force (dE/dx) well-known above 5-10 keV

CASINO (www.gel.usherb.ca/casino/index.html)

Ions: Stopping from both nuclear and electronic stopping
Electronic stopping much larger than nuclear
Quite accurate tabulations exist
Scattering mostly at low energies (< 10 keV)

SRIM (www.srim.org)

Sputtering: Grove’s experiment



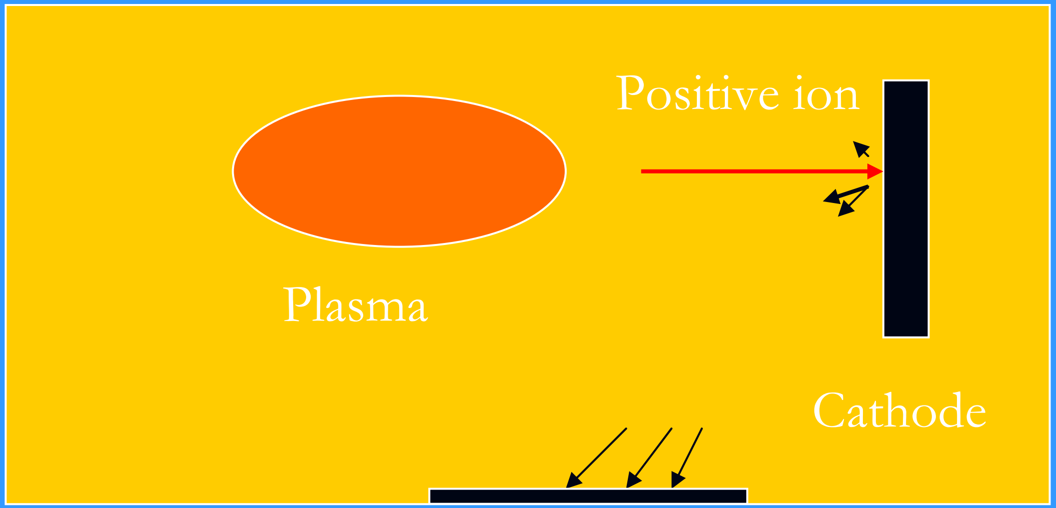
Positive ion

Plasma

Cathode

Discharge chamber

Sputtering: Grove's experiment

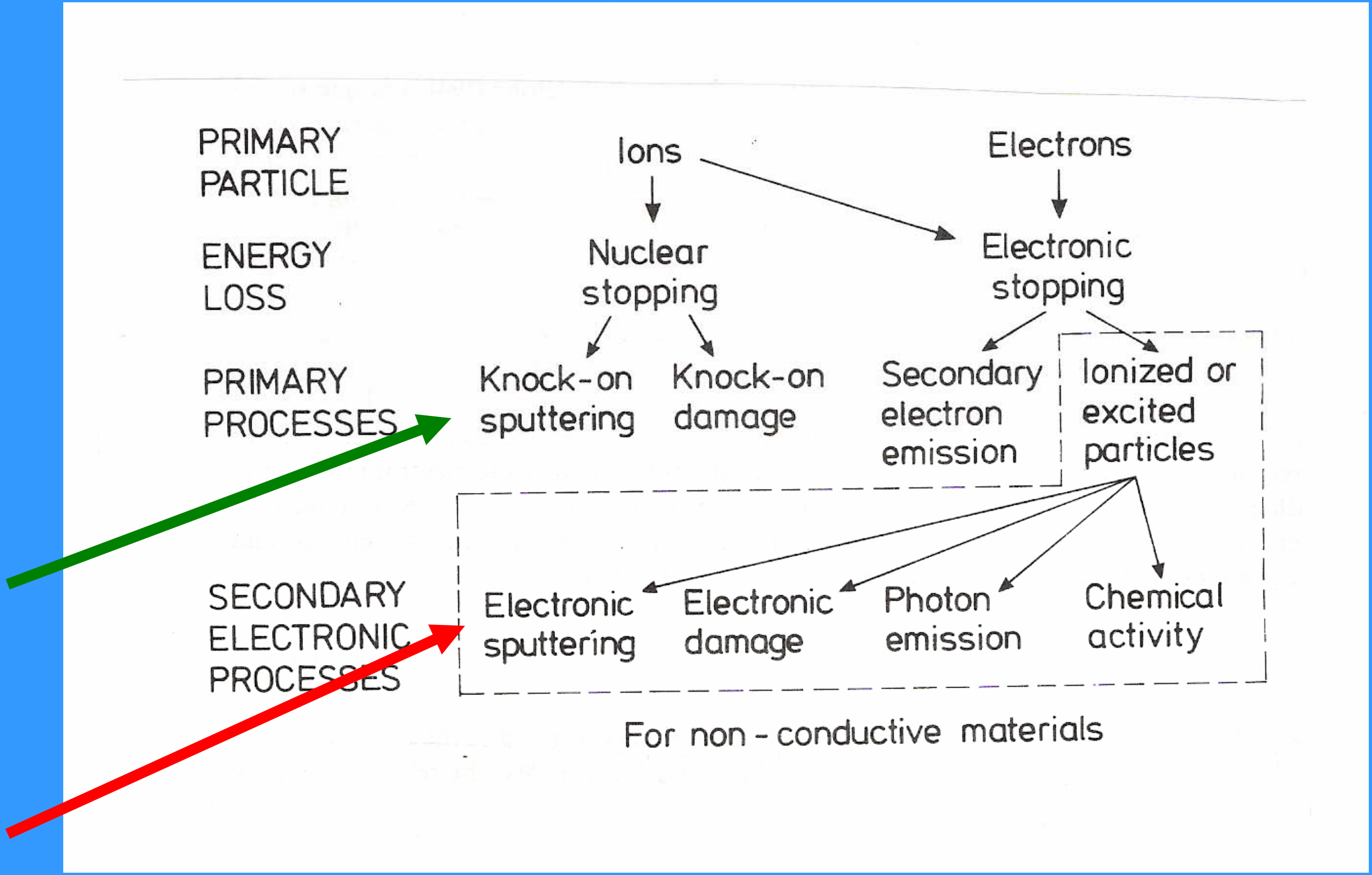


Discharge chamber

Layer of cathode material

Sputtered particles !

Energy loss and particle emission



PRIMARY PARTICLE

Ions

Electrons

ENERGY LOSS

Nuclear stopping

Electronic stopping

PRIMARY PROCESSES

Knock-on sputtering

Knock-on damage

Secondary electron emission

Ionized or excited particles

SECONDARY ELECTRONIC PROCESSES

Electronic sputtering

Electronic damage

Photon emission

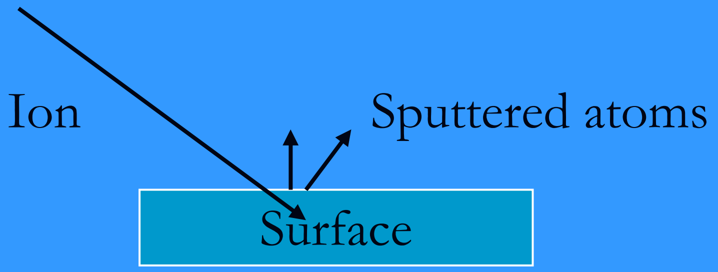
Chemical activity

For non-conductive materials

Sputtering: Particle ejection as a result of energetic particle bombardment

, Knock-on (Elastic, collsional) sputtering:

- Thin film production by sputtering deposition
- First wall interactions in fusion devices
- Materials analysis by SIMS



Sputtering:

Particle ejection as a result of energetic particle bombardment

Discovered by Grove in 1853

- Occurs for all solids
- Most features understood

Theory by Sigmund (1969) based on collision cascades.

Yield: $Y = \Lambda F_D(E,0)$ (Material constant × deposited energy)

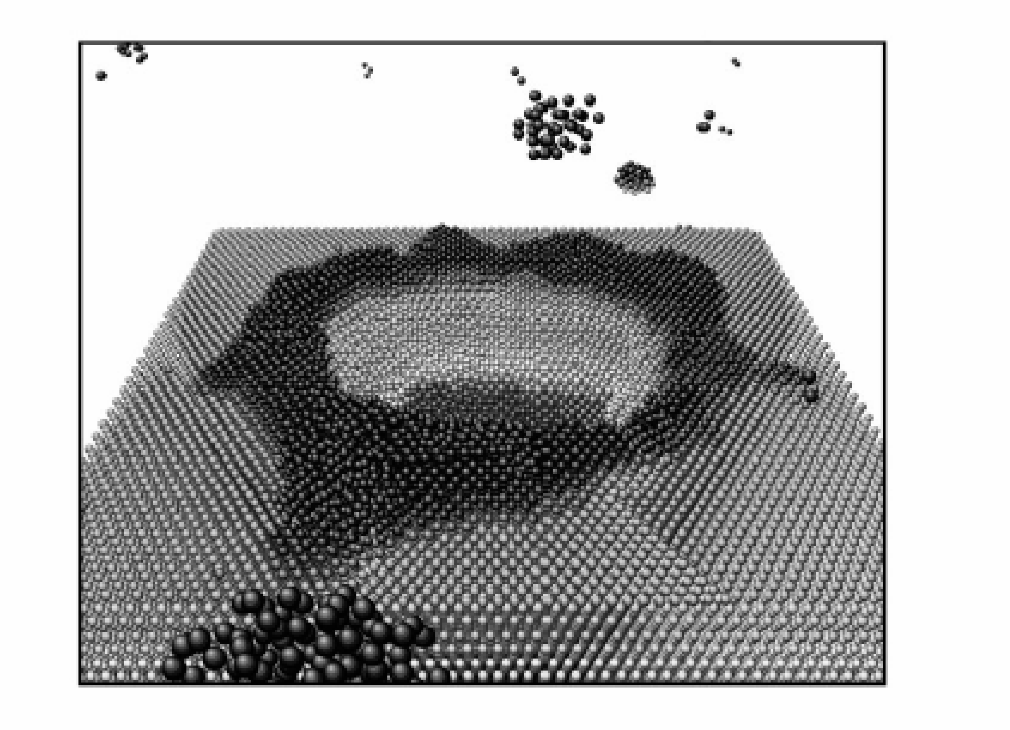
$F_D = \alpha\ (dE/dx)_n$ (sputtering α × nuclear stopping power)

$Y \sim U_o^{-1}$ (U_{0} : binding energy = sublimation energy)

Energy spectrum: $dY/dE_1 = k\ E_1/(E_1 + U_0)^3$

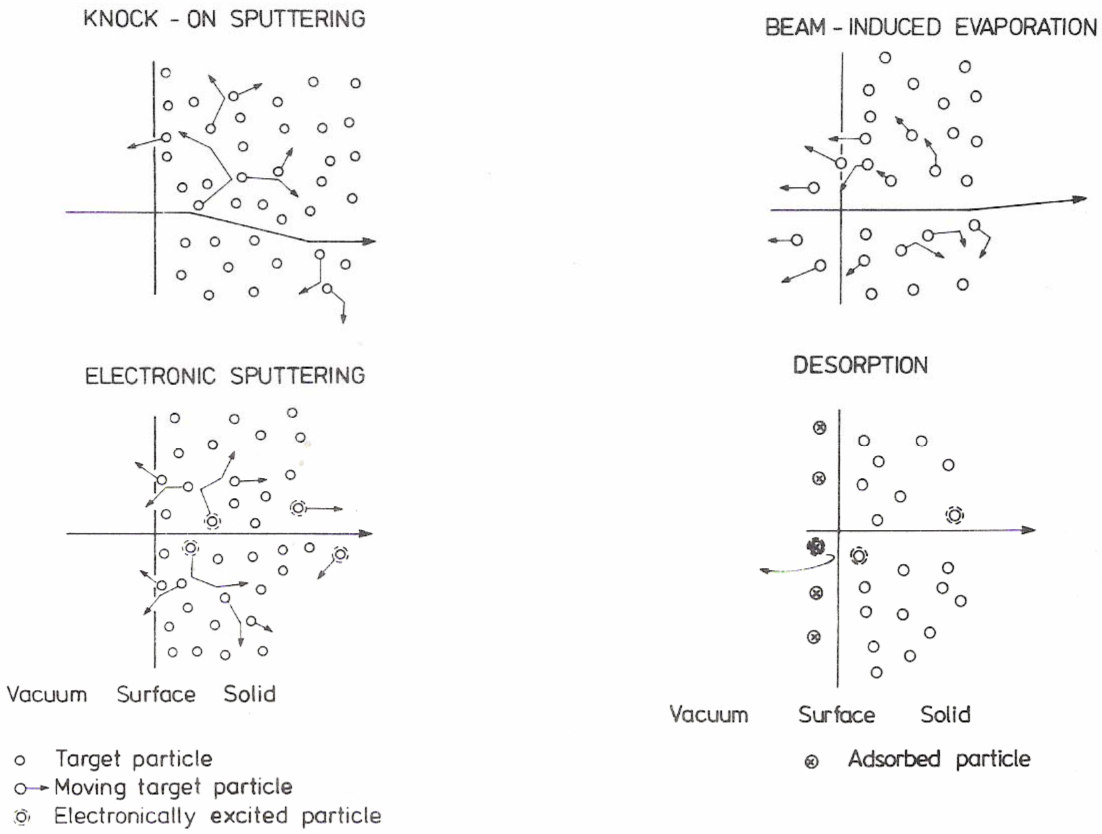
For large ejection energies E_1 : $dY/dE_1 \sim E_1^{-2}$

Sputtering of Au by a Au_{14} cluster



t = 40 ps , Y = 4759 Au-atoms/Au_{14}
From T. J. Colla and H. M. Urbassek, Nucl. Instr. Meth. B 164-165, 687 (2000)

Sputtering - desorption

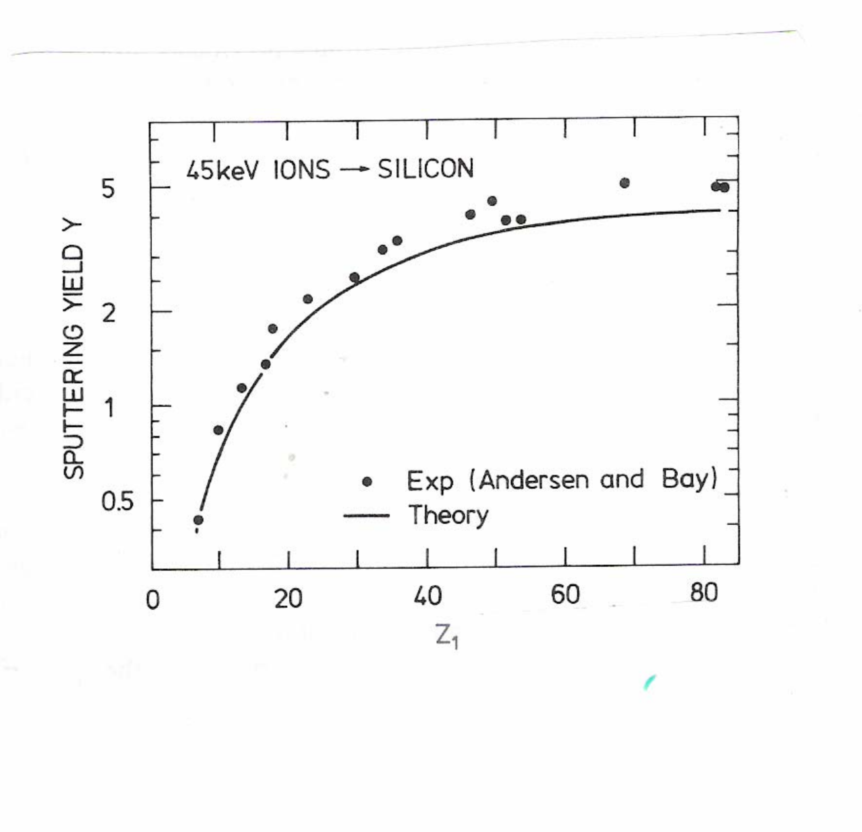


Sputtering: Particle ejection as a result of energetic particle bombardment

Theory by Sigmund (1969)
based on collision cascades.

Yield: $Y = \Lambda F_D(E,0)$
(Material constant × deposited energy)
$F_D = \alpha\ (dE/dx)_n$
(sputtering α × nuclear stopping power)
$Y \sim U_o^{-1}$
(U_0 : binding energy = sublimation energy)

Energy spectrum: $dY/dE_1 = k\ E_1/(E_1 + U_0)^3$
For large ejection energies E_1 : $dY/dE_1 \sim E_1^{-2}$



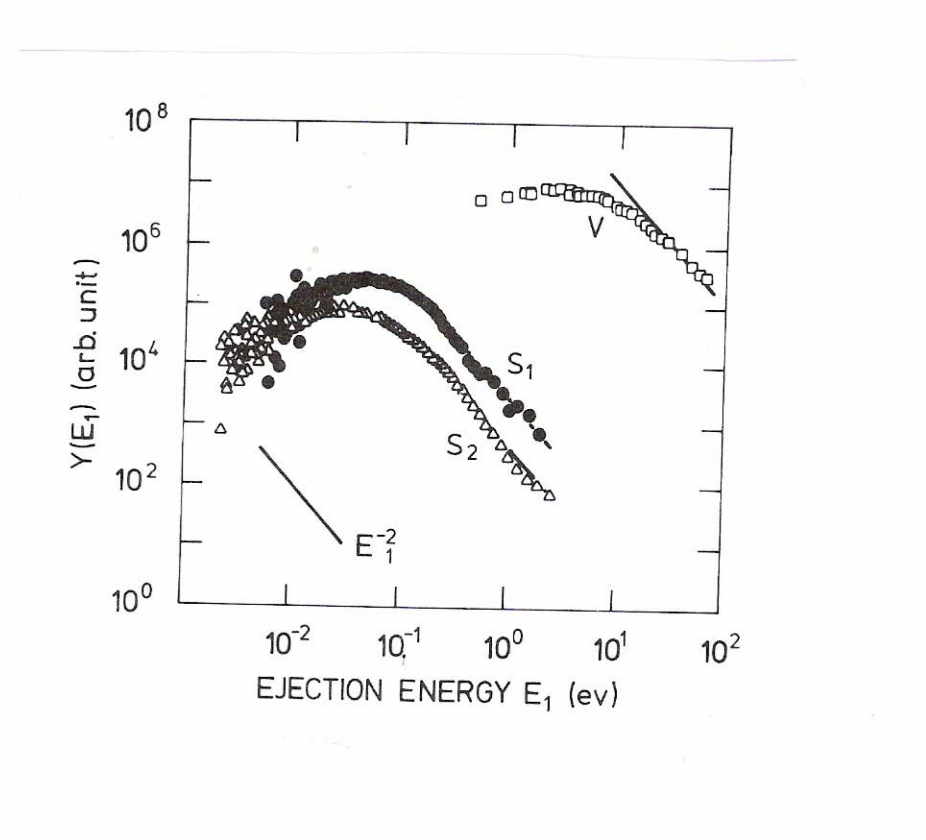
From H.H. Andersen and H. L. Bay, J. Appl. Phys. 46, 1919(1975).

Sputtering: Energy distribution of ejected particles

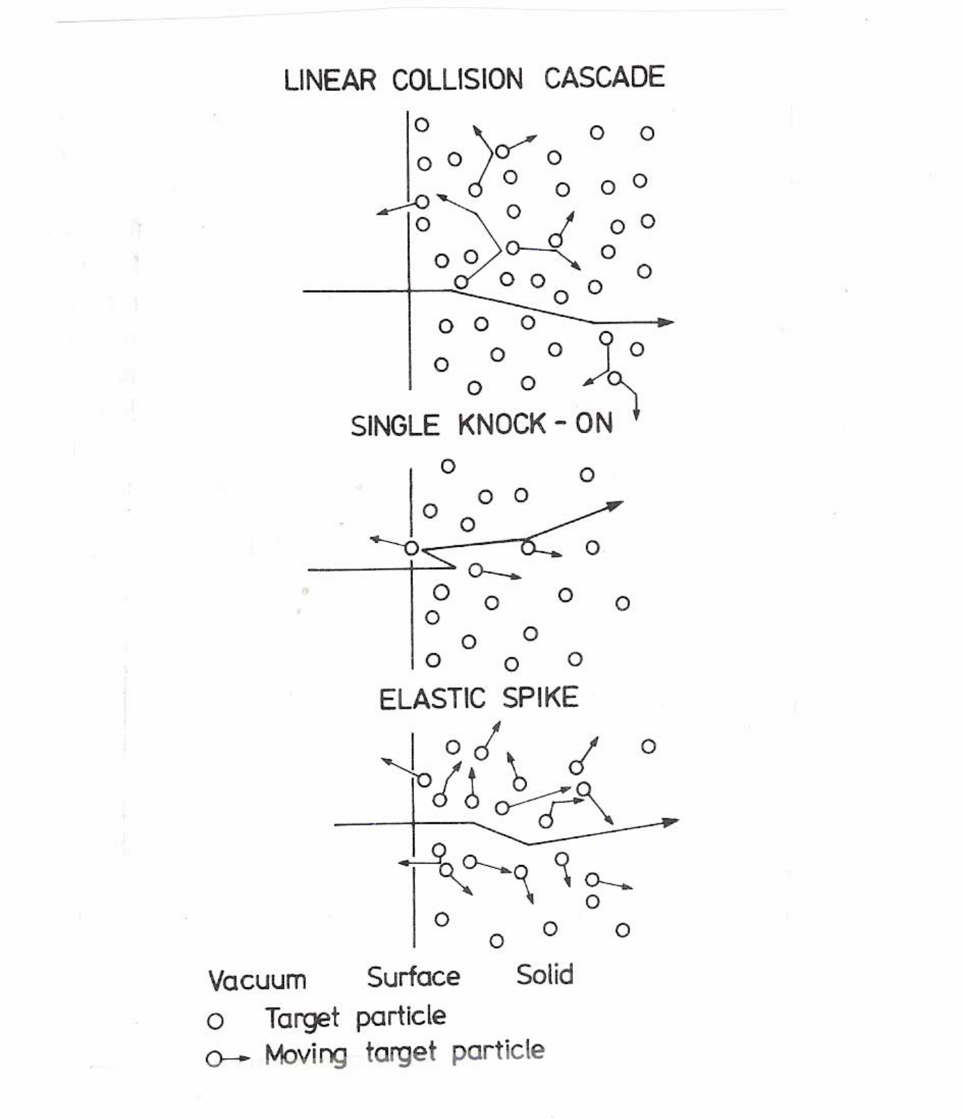
Theory by Sigmund (1969)
based on collision cascades.

(U_{0} : binding energy = sublimation energy)

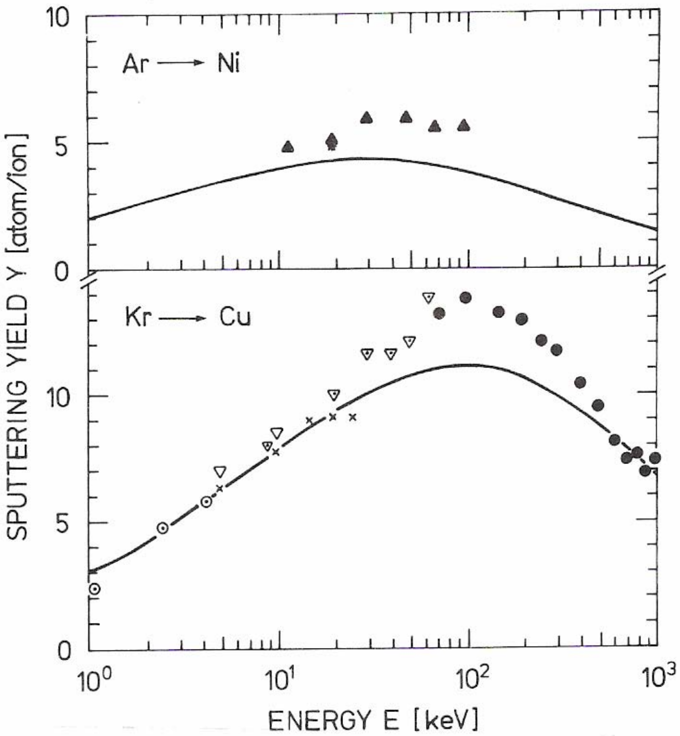
Energy spectrum: $dY/dE_1 = k\, E_1/(E_1 + U_0)^3$
For large ejection energies E_1 : $dY/dE_1 \sim E_1^{-2}$



Elastic sputtering (ions alone)



Outside the linear regime



Electronic sputtering (Multilayer desorption)

First important experiment on water ice 1978 by W. Brown et al.

- Occurs only for insulators (ices, alkali halides, refractory mat.)
- Requires localized energy which can be released non-radiatively
- In volatile solids (ices) low-energy cascades can be generated
- Some features understood

Yield: $Y = \frac{1}{2}\Lambda(E_s/W)D_e(E,0)$ (Material constant × deposited energy)
(E_s/W) (released transl. energy/energy per ionization)
$Y \sim U_o^{-1}$ (U_0 : binding energy = sublimation energy)

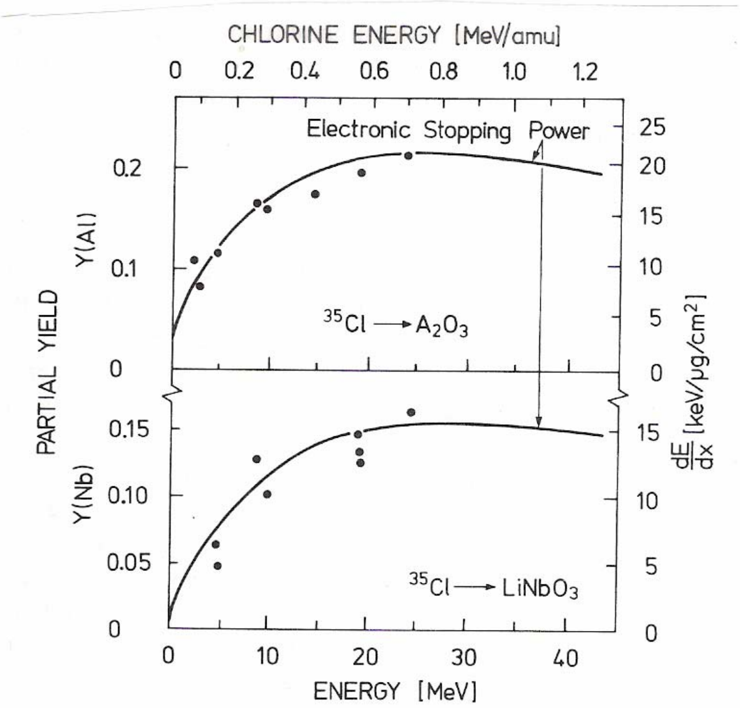
Energy spectrum: $dY/dE_1 = k\, E_1/(E_1 + U_0)^3$
For large ejection energies E_1 : $dY/dE_1 \sim E_1^{-2}$

Electronic sputtering (Multilayer desorption)

Important for ice bodies in planetary and insterstellar space
Ion and electron impact on cryogenic surfaces

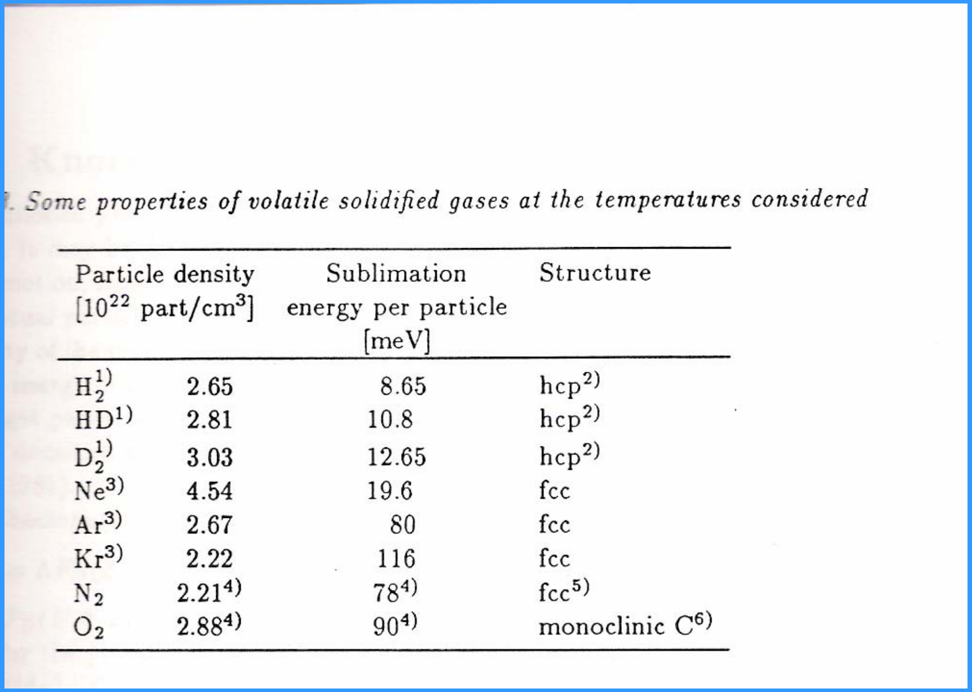
Heavy ions on insulators

Electronic sputtering refractory materials



From Y. Qui , J. E. Griffith and T. A. Tombrello, Rad. Eff. 64, 111 (1982)

Sublimation energy of ices



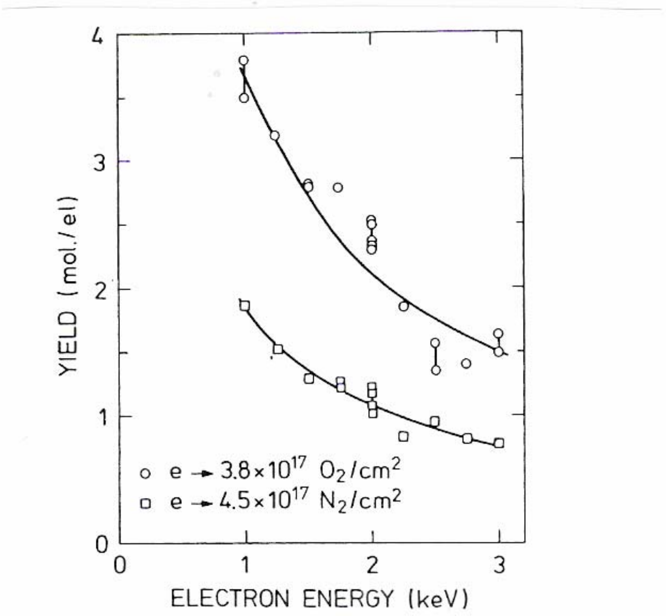
Some properties of volatile solidified gases at the temperatures considered

	Particle density [10^{22} part/cm^3]	Sublimation energy per particle [meV]	Structure
$H_2^{1)}$	2.65	8.65	hcp$^{2)}$
HD$^{1)}$	2.81	10.8	hcp$^{2)}$
$D_2^{1)}$	3.03	12.65	hcp$^{2)}$
Ne$^{3)}$	4.54	19.6	fcc
Ar$^{3)}$	2.67	80	fcc
Kr$^{3)}$	2.22	116	fcc
N_2	2.21$^{4)}$	78$^{4)}$	fcc$^{5)}$
O_2	2.88$^{4)}$	90$^{4)}$	monoclinic C$^{6)}$

Other values: Water ice 532 meV, metals. 3-6 eV

$Y \sim U_0^{-1}$ (U_0 : binding energy = sublimation energy)

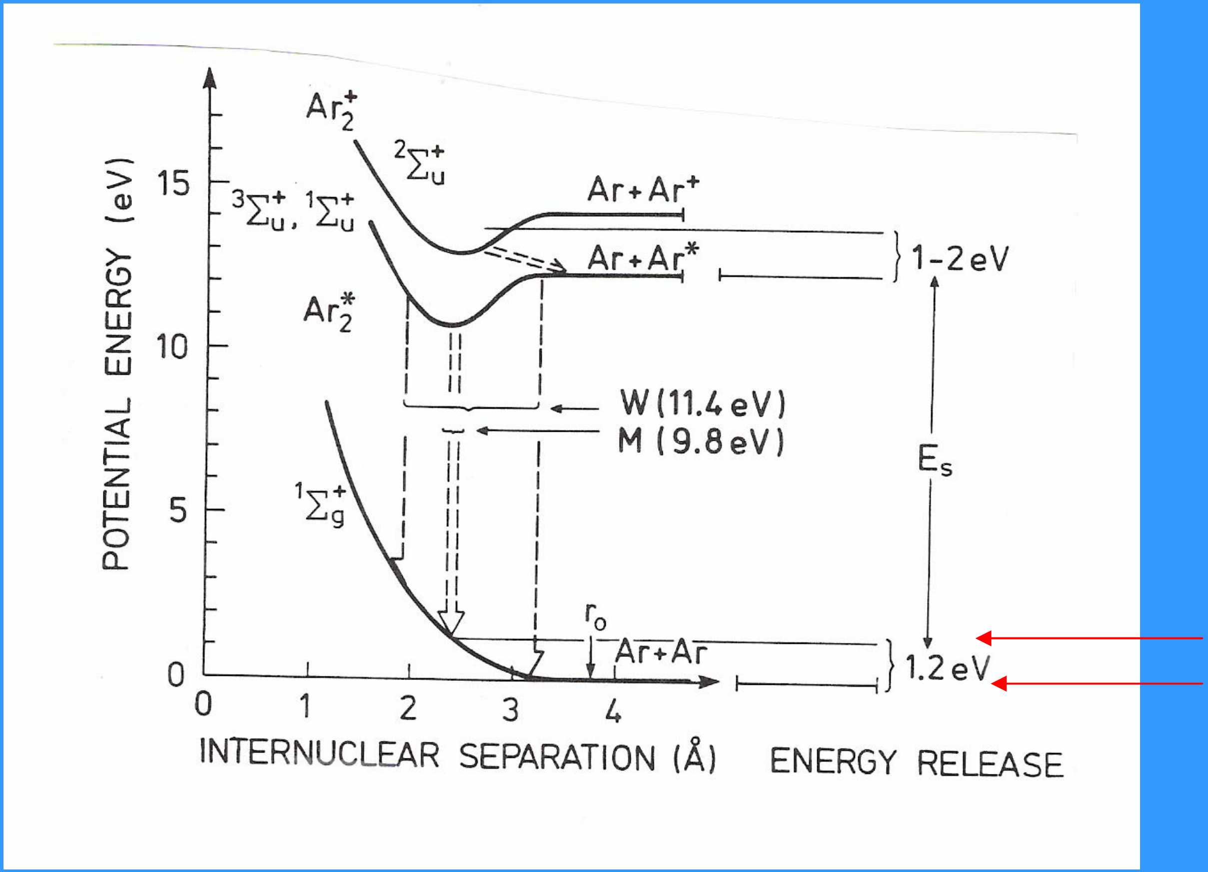
Electron sputtering: N_2 (keV primary electrons)



Not only ions, but also electrons can produce sputtering

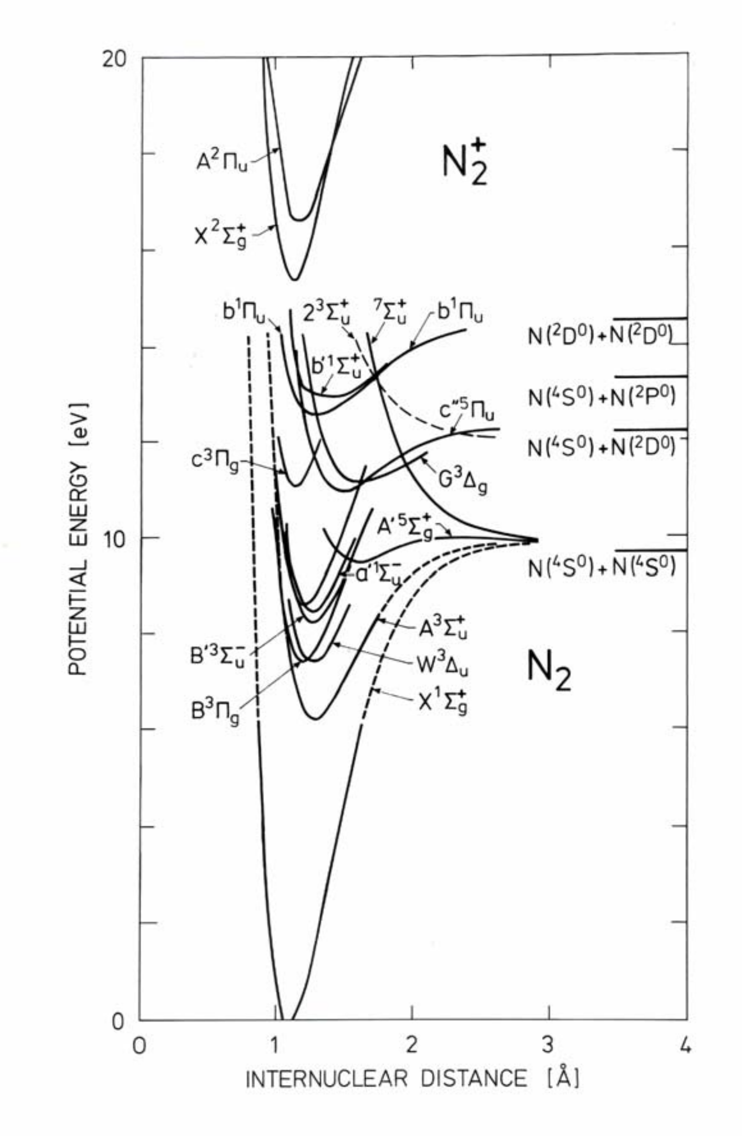
From O. Ellegaard, J. Schou, H. Sørensen and P. Børgesen, Surf. Sci. 167, 474 (1986)

Transitions in argon (for electronic sputtering)



Energy for ejection or cascades

Electronic sputtering: Transitions in N_2



From : O. Ellegaard et al., Surf. Sci. 302, 371 (1994).

H^+ and He^+ on solid CO

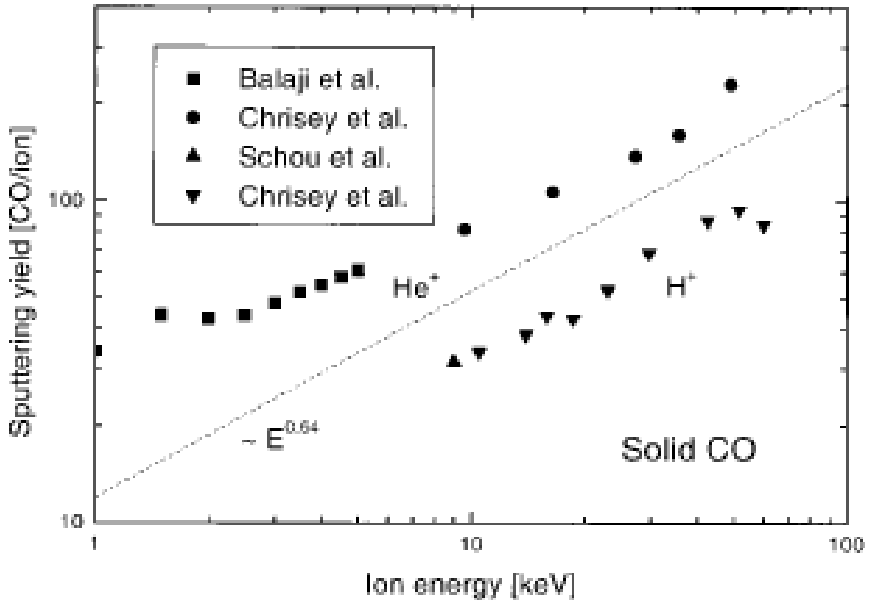


Figure 4. The sputtering yield as a function of energy for H^+ and He^+ ion bombardment. Data points from *Balaji et al.* [1995] and *Chrisey et al.* [1990] are shown as well. (The points from Chrisey et al. have been multiplied by a factor of 2.3; see text.)

$Y \sim S_e(E)$:
Electronic sputtering !

From. J. Schou and R. Pedrys, J. Geophys. Res. 106, E12, 33309 (2001).

Spectrum from solid CO

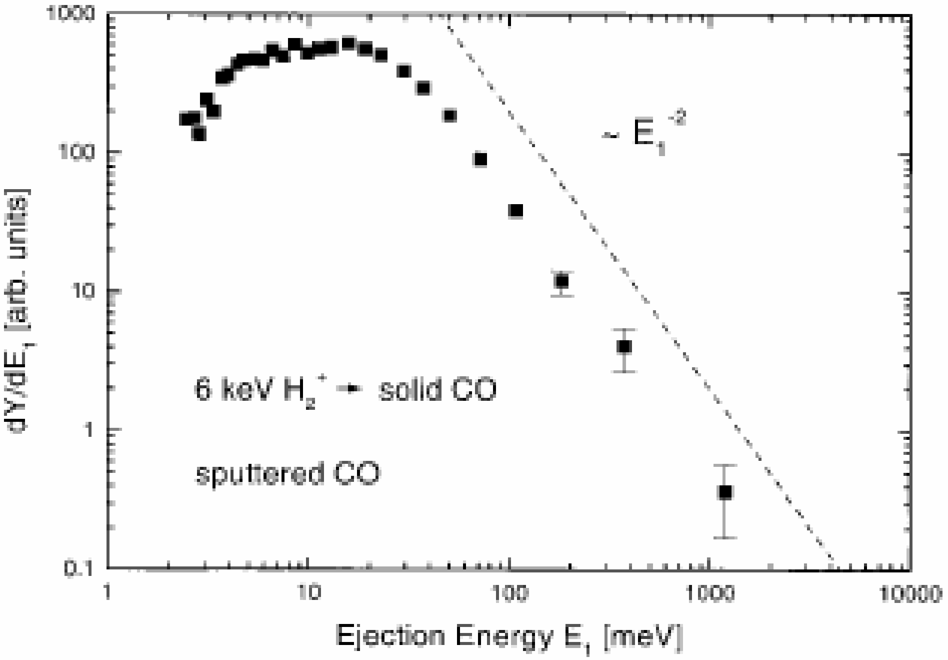


Figure 7. Energy distribution of CO molecules as a function of energy E_1 sputtered from solid CO by 6 keV H_2^+ ions at an angle of incidence of 60°. The dashed line indicates the asymptotic E_1^{-2} tail representative of linear collision cascades.

From J. Schou and R. Pedrys, J. Geophys. Res. 106, E12, 33309 (2001)

Water ice: Yield

Knock-on and electronic sputtering

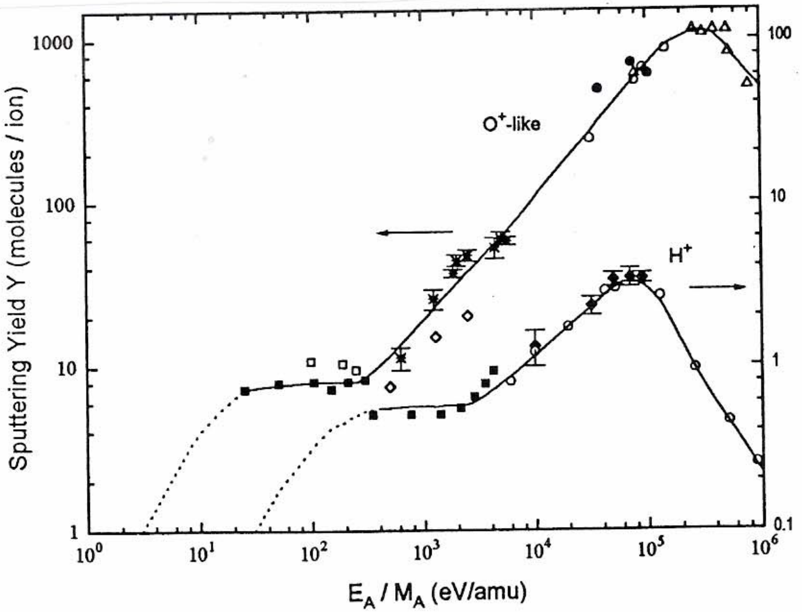


Figure 4. Compilation of sputtering yields for incident H^+ and oxygen-like ions from Table 1: open circles, H^+ [*Brown et al.*, 1980a, b], C^+, O^+ [*Brown et al.*, 1982]; solid circle, N^+ [*Bøttiger et al.*, 1980]; open triangle, F^{+q} [*Cooper and Tombrello*, 1984]; solid square, H_2^+, Ne^+ [*Bar-Nun et al.*, [1985]; open diamonds, Ne^+ [*Chrisey et al.*, 1986]; open squares, N^+, Ne^+ [*Christiansen et al.*, 1986]; solid diamonds, H^+ [*Shi et al.*, 1995]; asterisks, O^+ (this work). Solid lines are guides for the eye. Dashed lines are extrapolations based on estimated nuclear stopping power.

From M. Shi, R. A. Baragiola, D. E. Grosjean, R. E. Johnson, S. Jurac and J. Schou, J. Geophys. Res. 100, E12, 26387 (1995)

Water ice: Yield

Knock-on and electronic sputtering

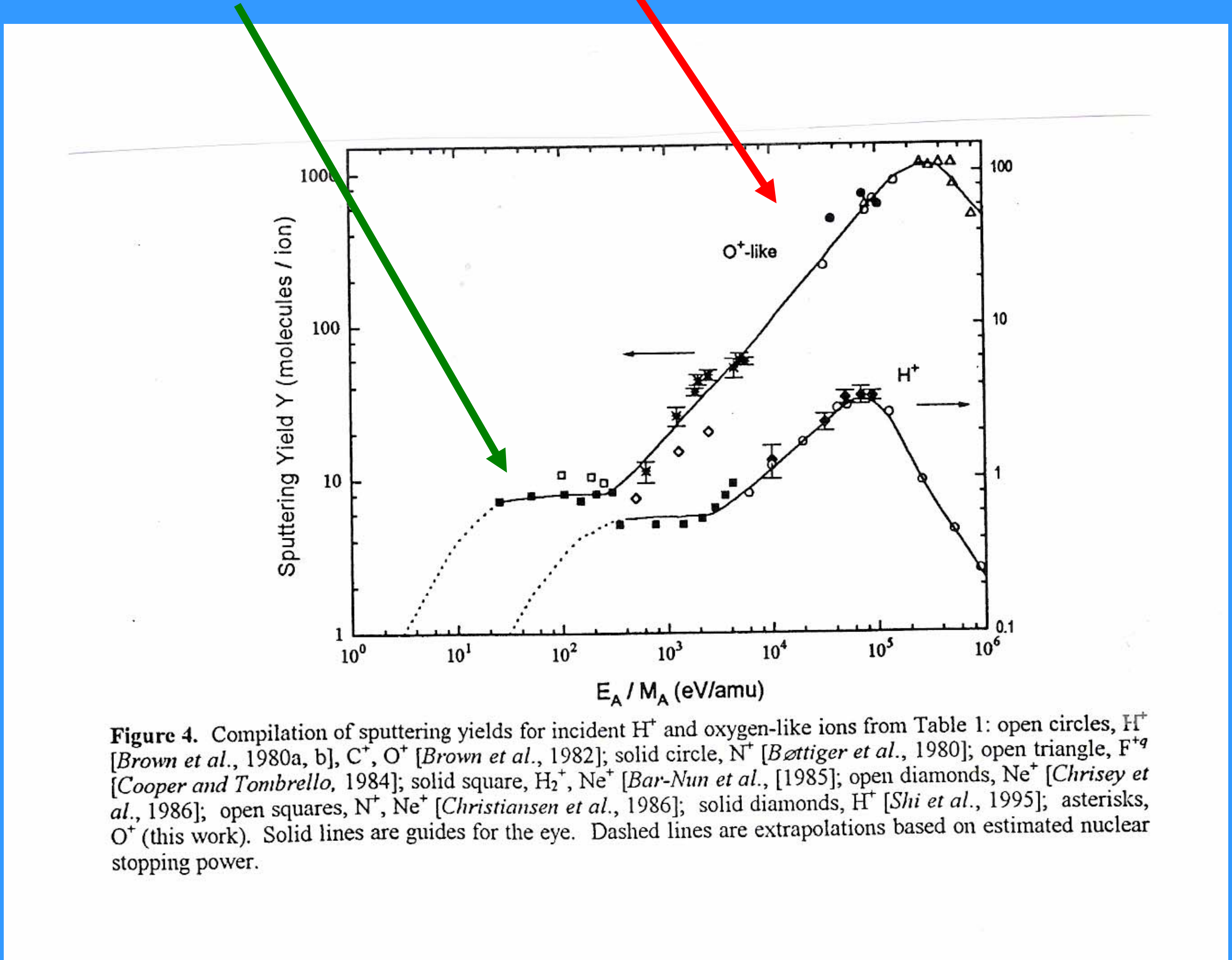


Figure 4. Compilation of sputtering yields for incident H$^+$ and oxygen-like ions from Table 1: open circles, H$^+$ [*Brown et al.*, 1980a, b], C$^+$, O$^+$ [*Brown et al.*, 1982]; solid circle, N$^+$ [*Bøttiger et al.*, 1980]; open triangle, F^{+q} [*Cooper and Tombrello*, 1984]; solid square, H$_2^+$, Ne$^+$ [*Bar-Nun et al.*, [1985]; open diamonds, Ne$^+$ [*Chrisey et al.*, 1986]; open squares, N$^+$, Ne$^+$ [*Christiansen et al.*, 1986]; solid diamonds, H$^+$ [*Shi et al.*, 1995]; asterisks, O$^+$ (this work). Solid lines are guides for the eye. Dashed lines are extrapolations based on estimated nuclear stopping power.

Y is prop. to

$S_e(E)^2$!

From M. Shi, R. A. Baragiola, D. E. Grosjean, R. E. Johnson, S. Jurac and J. Schou, J. Geophys. Res. 100, E12, 26387 (1995)

Electronic sputtering of water ice: Lyman-α photons

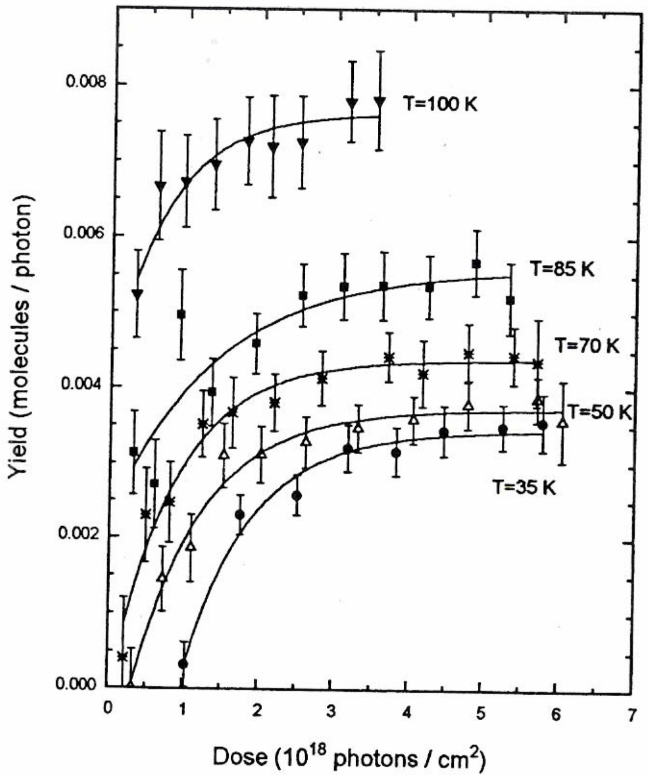
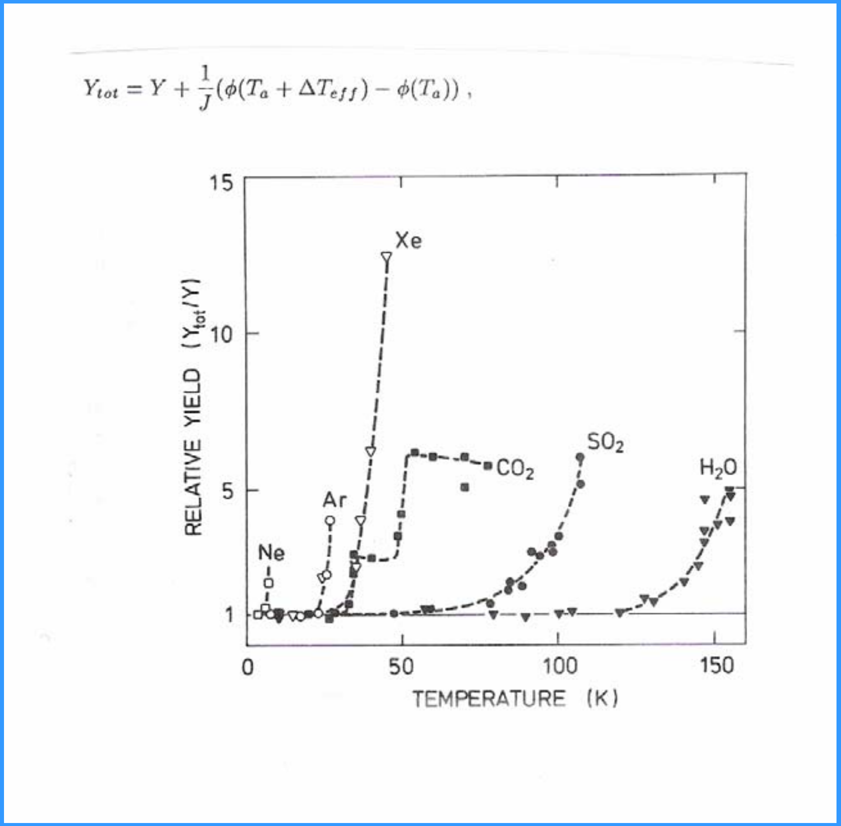


Figure 5. Photosputtering yield of water ice versus fluence (photons/cm^2) for Lyman-a photons. Curves are rough fits to data at different temperatures [from *Westley et al.*, 1995].

Beam-induced evaporation
Ions, electrons and photons



$$Y_{tot} = Y + \frac{1}{J}(\phi(T_a + \Delta T_{eff}) - \phi(T_a)) \, ,$$

Beam heating most pronounced for volatile solids

Thin films: sputtering/desorption

Electronic sputtering of thin cryogenic layers

S. K. Erents and
G. M. McCracken,
J. Appl. Phys. 44, 3139 (1973)

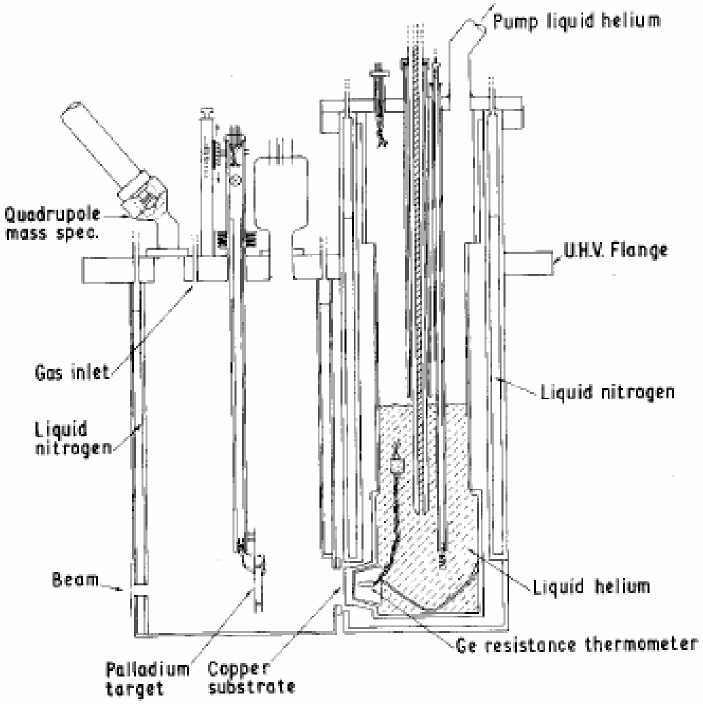
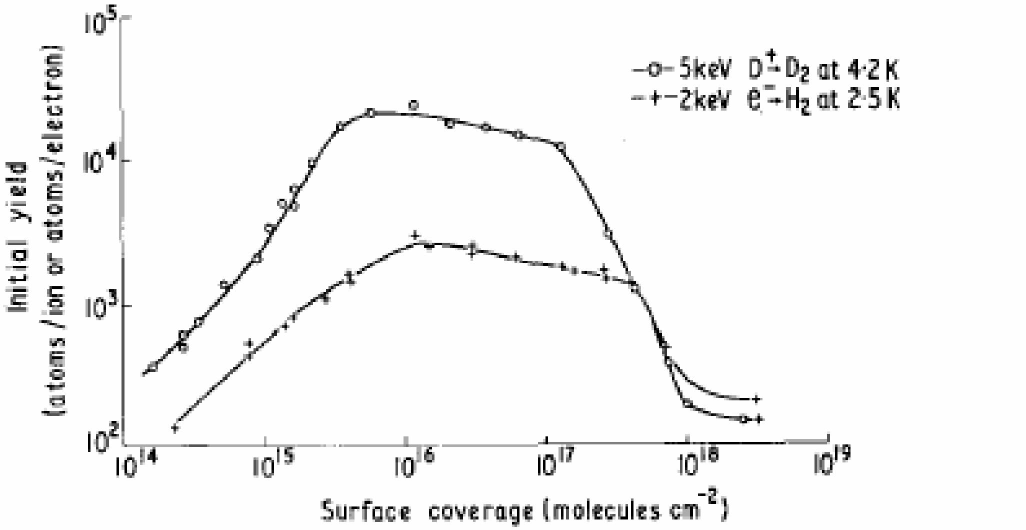


FIG. 1. Schematic diagram of the target chamber and helium cryostat.



Protons on solid CO
No thickness dependence

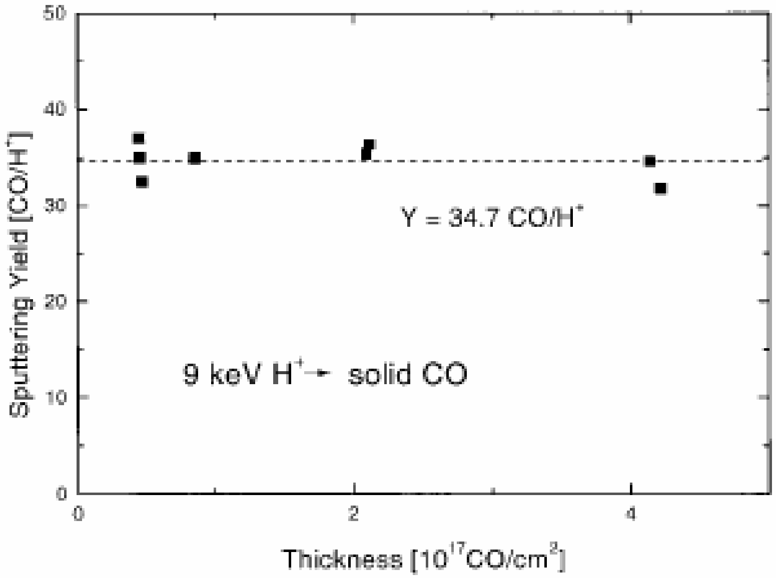
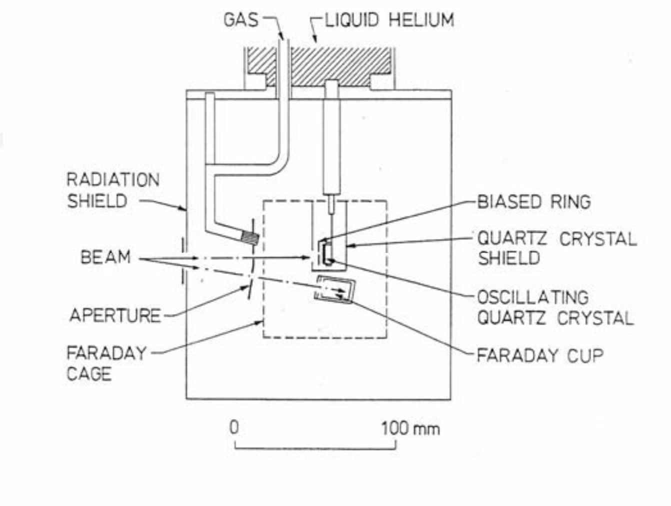


Figure 2. The sputtering yield as a function of CO film thickness for 9 keV H$^+$. The dashed line shows the average yield $Y = 34.7$ CO/H$^+$. All films have been deposited on residues less than 18×10^{15} eq CO molecules/cm^2.



From J. Schou and R. Pedrys, 106, E12, 33309 (2001)

Thickness dependence of Ne: (primary electrons)

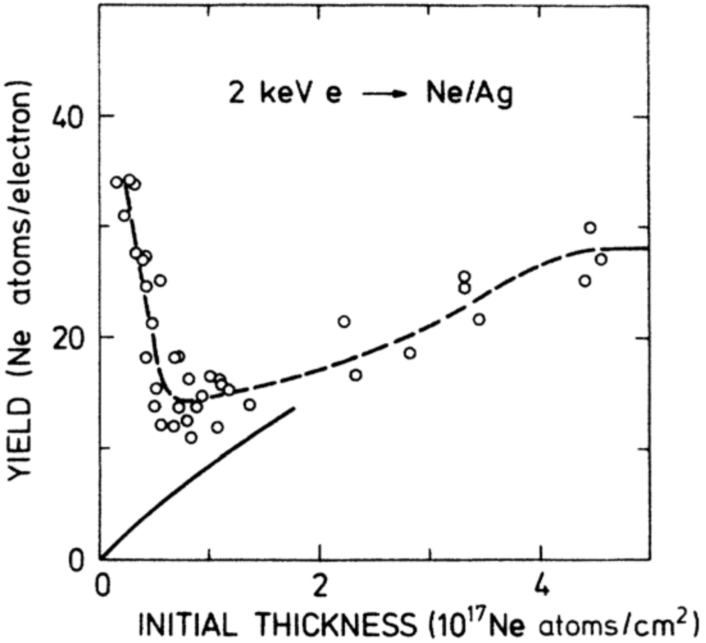
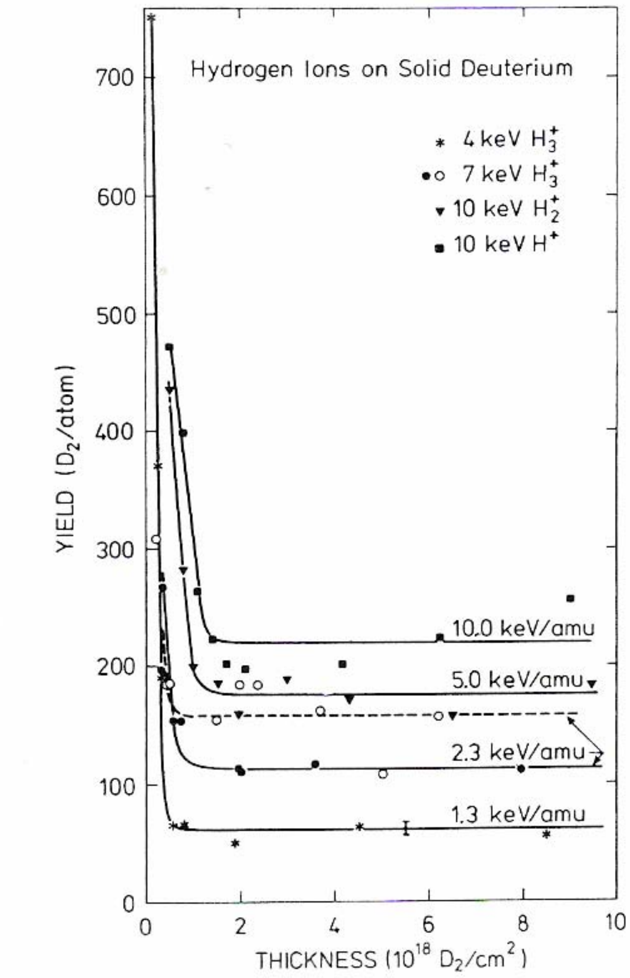


FIG. 5. Sputtering yield of solid neon resulting from bombardment of 2-keV electrons measured by the frequency-change method. The yield is plotted versus the initial thickness. The silver electrode of the crystal serves as a substrate. — — —, curve drawn to guide the eye. ——, Eq. (20) with $ff_e=3$ and $l_0=1\times10^{17}$ Ne atoms/cm^2.

From : J. Schou, P. Børgesen, O.Ellegaard, H. Sørensen and C. Claussen, Phys. Rev. B 34, 93 (1986).

Electronic sputtering D_2: (hydrogen and He ions)



From : B. Stenum, O. Ellegaard, J. Schou and H. Sørensen, Nucl. Instr. Meth.B 48 530 (1990)

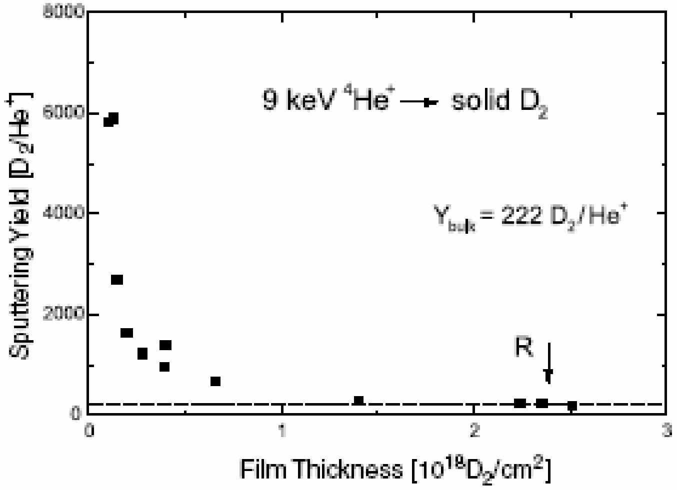


Fig. 4. Sputtering yield as a function of film thickness for 9 keV $^4He^+$ incident on solid deuterium (1×10^{18} D_2 molecules/cm^2 = 3310 Å for a homogeneous film). *R* is the average projected range of the ion [3].

Electronic sputtering-desorption

Occurs only for the most volatile solids

It is clearly induced by electronic transitions – in substrate or in the film

Induced by electron, light ions or light

It is most pronounced for the most volatile ices

Conclusion: Sputtering

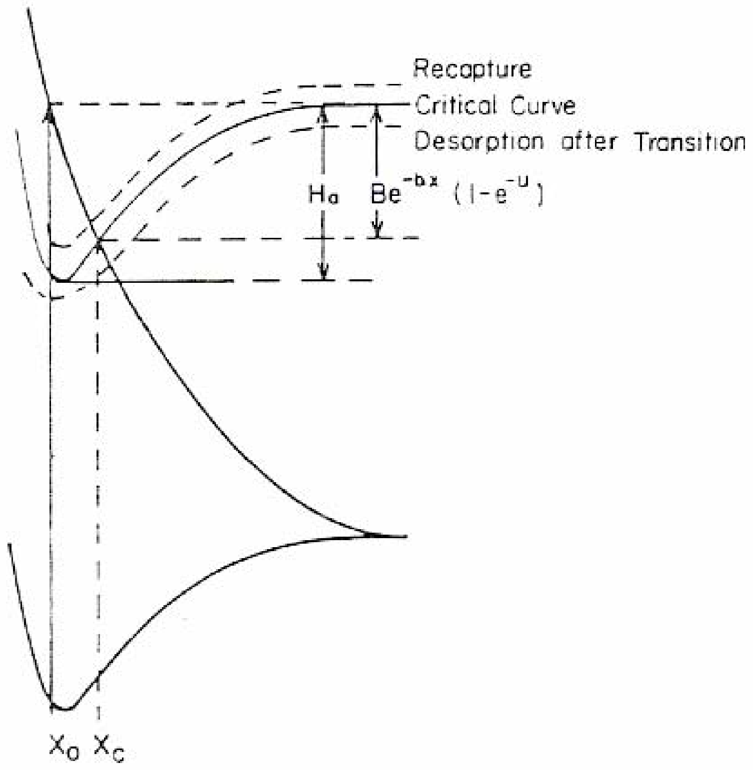
*Magnitude of sputtering correlated to stopping force
*Sputtering of elemental targets (conducting) is well understood.
*Condensed gases have efficient energy transfer mechanisms
*Water ice is particularly difficult to understand even after 20 years
’In general, chemical reactions complicate the picture
*Desorption of less than one monolayer seems less efficient

Thank you for your attention

The MGR model

Menzel-Gomer-Redhead (1964)

Desorption induced by electronic transitions - DIET



Desorption cross section:

$\sigma = \sigma_e P$

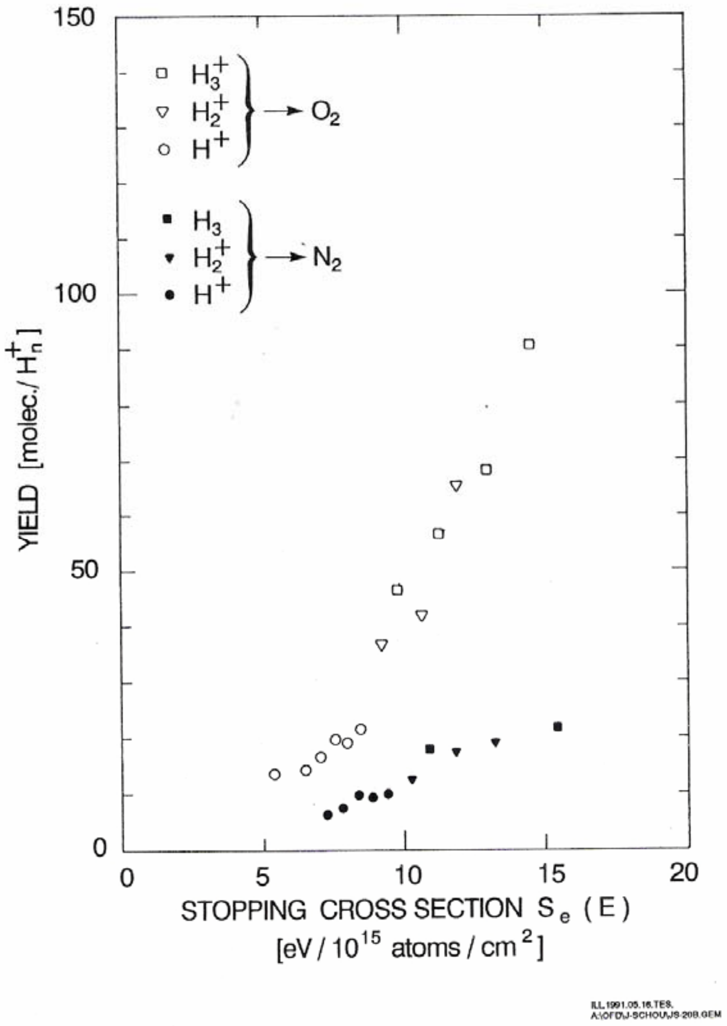
P: escape probability

σ_e: primary excitation cross section

$P = \exp(-cM^{1/2})$

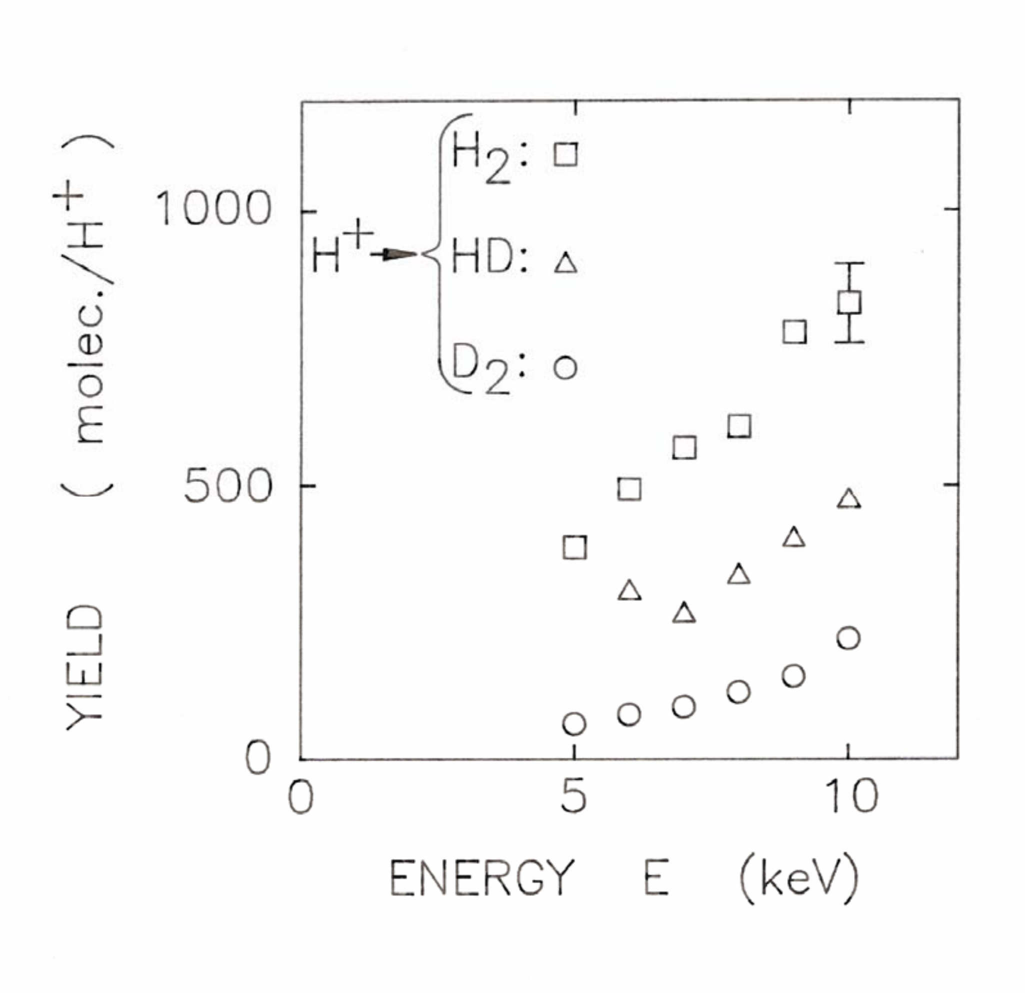
M is molecular weight

Electronic sputtering: N_2 and O_2 (primary hydrogen ions)



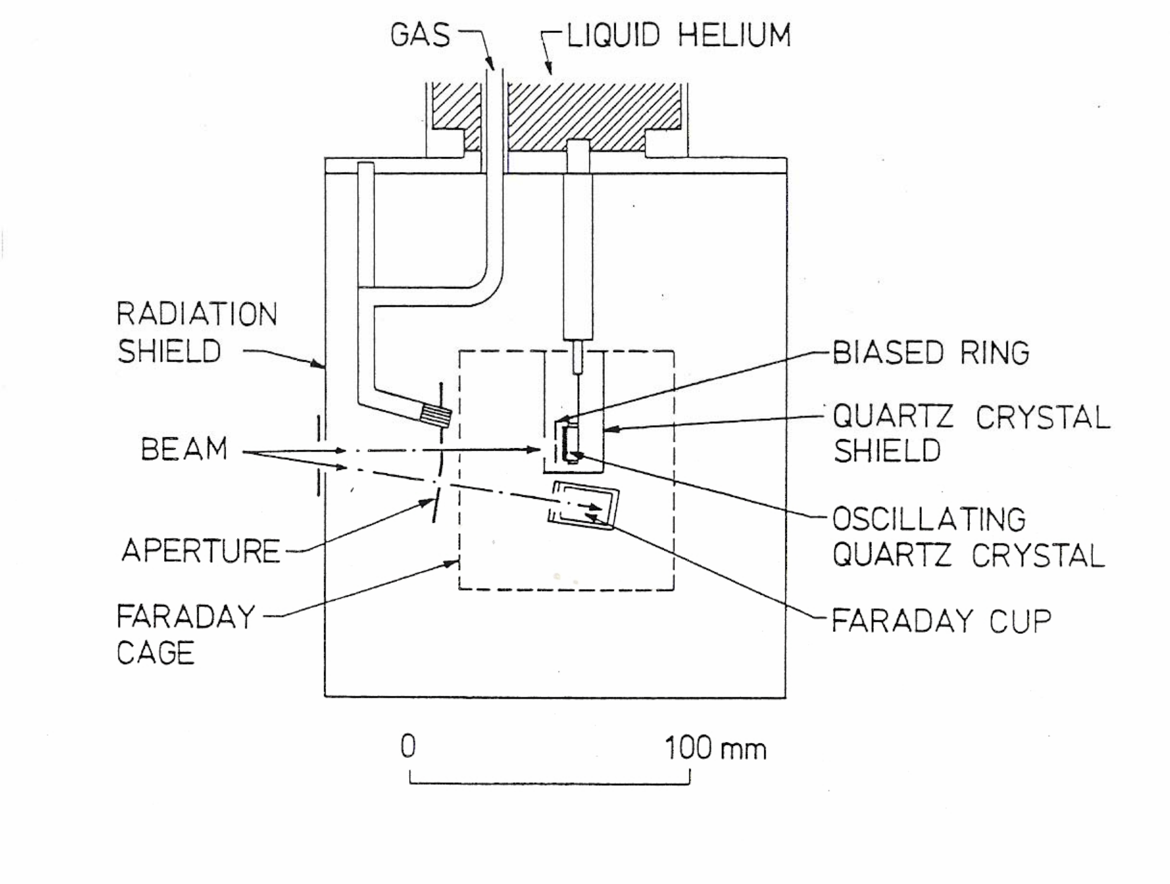
From : O. Ellegaard et al., Surf. Sci.302, 317 (1994)

Ion bombardment of hydrogenic solid



From B. Stenum, J. Schou, O. Ellegaard, H. Sørensen and R. Pedrys, Phys. Rev. Lett. 67, 2842 (1991).

Setup at Risø



Electron beam: 0.5 – 3 keV
Ion beam 4 – 10 keV (mostly light ions)

Quartz crystal microbalance
1 Hz ~1.29 10^{16} amu/cm^2.

Risø National Laboratory, OFD

Light absorption in gold