X. Erfahrungsaustausch
Oberflächentechnologie mit Plasma- und Ionenstrahlprozessen
Mühlleithen 2003

Ion Bombardment from Low-Pressure Plasmas

Tutorial

Wolfhard Möller

Institute of Ionen Beam Physics and Materials Research
Forschungszentrum Rossendorf, Dresden, Germany

- Plasma Sheath and Energetic Ion Fluxes
- Surface Processes
- Ion Bombardment and Thin Film Deposition

Plasma Sheath and Energetic Ion Fluxes

Reading

M. A. Lieberman and A. J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing*. New York: John Wiley & Sons, 1994.

A.Anders (Ed.), *Handbook of Plasma Immersion Ion Implantation and Deposition.*
New York, John Wiley & Sons, 2000.
(Chapter 2 by M.A. Lieberman; Chapter IV by B.P. Wood et al.)

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Plasma Sheath and Presheath (Collisionless)

High mobility of electrons → **Plasma charges positively**

Sheath electrostatic potential

$$\frac{d^2F(x)}{dx^2} = \frac{e}{e_0}\left(n_e - n_i\right)$$

Boltzmann distribution of electrons

$$n_e(x) = n_s e^{\frac{F(x)}{kT_e}}$$

Conservation of ion energy

$$m_i u^2(x) = m_i u_s^2 - 2eF(x)$$

u Ion velocity

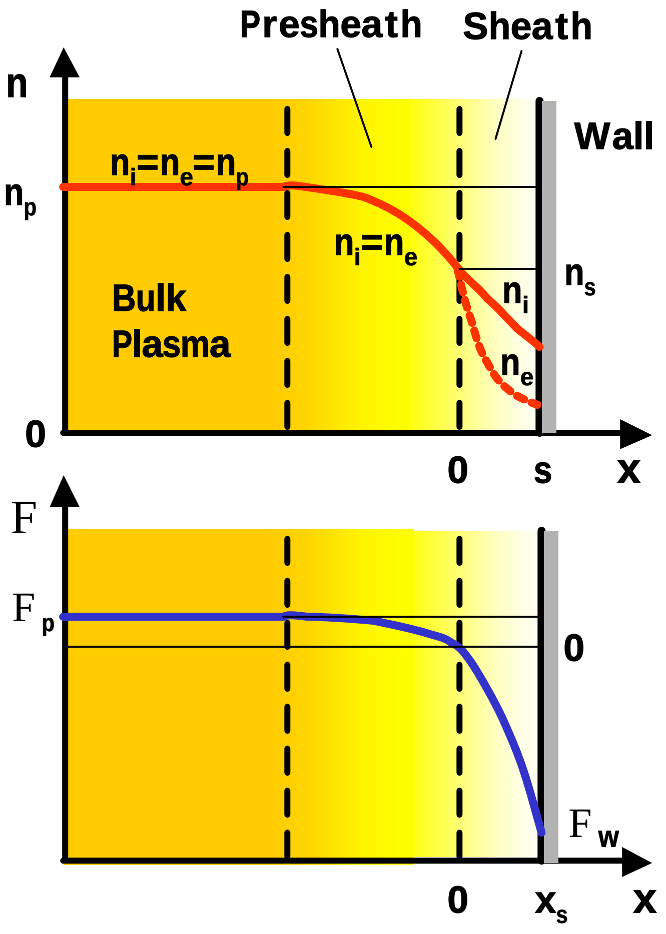
Conservation of ion flux

$$n_i(x)\,u(x) = n_s u_s$$

↓

Sheath potential equation

$$\frac{d^2F(x)}{dx^2} = \frac{en_s}{e_0}\left(e^{F(x)/kT_e} - \left(1 - \frac{2F(x)}{m_i u_s^2}\right)\right)$$



Ion Energy and Flux to Wall (Collisionless, Floating Wall)

Stable solution for sheath potential only for

Bohm criterion

$$u_s \geq u_B = \sqrt{\frac{kT_e}{m_i}}$$

u_B Bohm or ion acoustic velocity

It can be shown that Bohm criterion holds marginally

$$u_s = u_B$$

Presheath energy conservation

$$m_i u_B^2 = 2e\Phi_p$$

➡ $$\Phi_p = \frac{kT_e}{2e}$$

Sheath edge density

$$n_{is} = n_{es} = n_p e^{-\Phi_p / kT_e} = e^{-1/2} n_p$$

➡ $$j_i = e^{-1/2} n_p \sqrt{\frac{kT_e}{m_i}}$$

Charge conservation in sheath

$$n_s u_B = j_{is} = j_{ew} = \frac{1}{4} n_s \sqrt{\frac{8kT_e}{\pi m_e}} e^{\Phi_w / kT_e}$$

➡ $$\Phi_w = -\frac{kT_e}{2e} \ln\left(\frac{m_i}{2\pi m_e}\right)$$

Floating potential

$$\Phi_{fl} = \Phi_p - \Phi_w$$

Ion energy at wall

$$E_i = e\Phi_{fl} = \frac{kT_e}{2}\left(1 + \ln\left(\frac{m_i}{2\pi m_e}\right)\right)$$

Example: CH_4

CH_4^+ and CH_3^+ ions
$n_e = 5 \cdot 10^{10}$ cm^{-3}
$kT_e = 1.1$ eV

$j_i = 7.8 \cdot 10^{15}$ cm^{-2}s^{-1}

$E_i = 5.2$ eV

Floating and High Voltage DC Sheaths (Collisionless)

From sheath potential equation and $\Phi(x_s) = \Phi_w$

Floating sheath thickness

$$x_s \approx 2\ldots5\,\lambda_{Debye} = 2\ldots5\sqrt{\frac{\varepsilon_0 kT_e}{n_p e^2}}$$

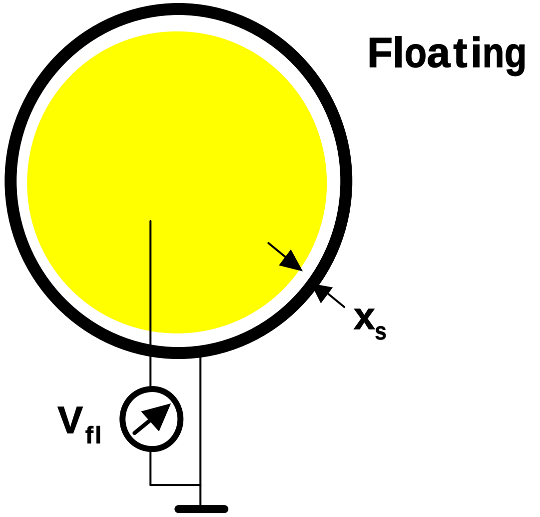
For high voltage $V_0 \gg e^{-1}kT_e$ applied to electrode, Child-law ion flux equals Bohm flux

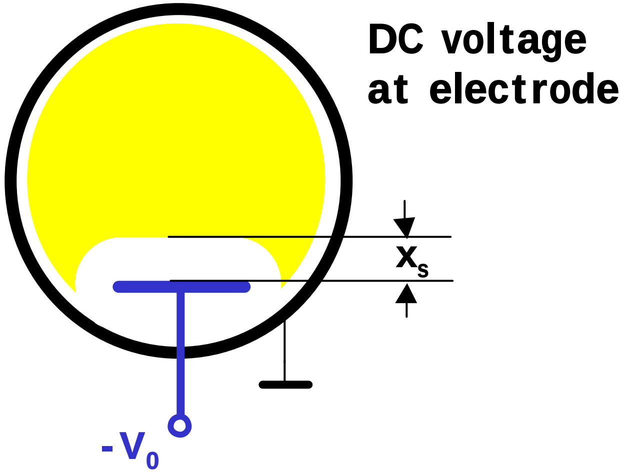
$$e^{-\frac{1}{2}} n_p \sqrt{\frac{kT_e}{m_i}} = j_i = \frac{4\varepsilon_0}{9e}\sqrt{\frac{2e}{m_i}}\,\frac{V_0^{3/2}}{x_s^2}$$

Langmuir-Child sheath thickness

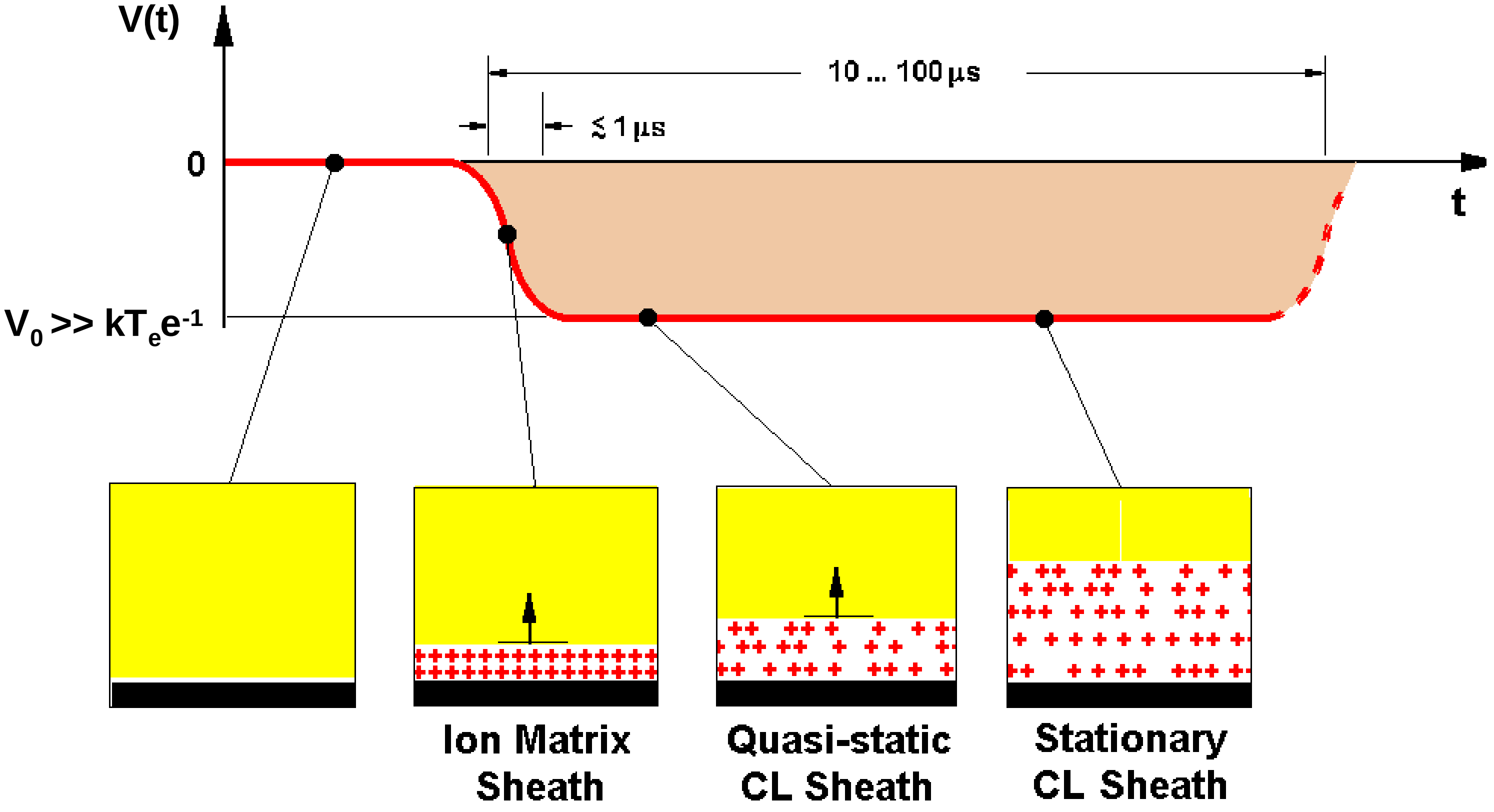
$$x_s = \frac{\sqrt{2}}{3} e^{\frac{1}{4}} \lambda_D \left(\frac{2eV_0}{kT_e}\right)^{\frac{3}{4}}$$

x_s adjusts to V_0 at constant ion flux
V_{fl} is not significantly altered if electrode area is small compared to total wall area





Pulsed DC High Voltage Transient Sheaths (Collisionless) ("Plasma Immersion Ion Implantation")



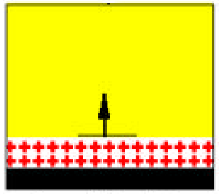
Ion Matrix Sheath

- Initially and for quickly rising pulses, electrons are pushed into plasma, whereas ions reside due to their inertia

Time Scale $t_M \gg w_{pe}^{-1} = \sqrt{\frac{e_0 m_e}{n_p e^2}}$ w_{pe} Electron plasma frequency

From electrostatics

Matrix sheath thickness $x_{sM} = l_{Debye}\sqrt{\frac{2eV}{kT_e}} = \sqrt{\frac{2e_0 V}{n_p e}}$



Ion Matrix Sheath

- Subsequently, ions are extracted from matrix sheath

Time Scale $t_{ME} \gg w_{pi}^{-1} = \sqrt{\frac{e_0 m_i}{n_p e^2}}$ w_{pi} Ion plasma frequency

Ion energies are distributed according to different positions of origin

Ion energy distribution function $f(E_i) = \frac{1}{2\sqrt{eVE_i}}$

Quasi-Static Langmuir-Child Sheath

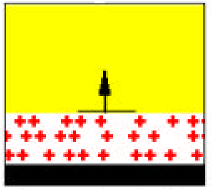
- After ion extraction from matrix sheath, the sheath expands further. The instantaneous ion fluxes are approximated by the Child law

Time Scale $\tau_{QLC} >> \omega_{pi}^{-1} = \sqrt{\frac{\varepsilon_0 m_i}{n_p e^2}}$ ω_{pi} Ion plasma frequency

Additional ion flux from “peeling off” the plasma boundary

Ion flux balance

$$e^{-1/2} n_p \left(\sqrt{\frac{kT_e}{m_i}} + \frac{dx_s}{dt} \right) = j_i = \frac{4\varepsilon_0}{9e} \sqrt{\frac{2e}{m_i}} \frac{V_0^{3/2}}{x_s^2}$$



Quasi-static CL Sheath

- Finally, sheath converges towards stationary LC sheath thickness

- Ion energy corresponds to full voltage. For ideally rectangular pulses

Ion energy distribution function

$$f(E_i) = \delta(E_i - eV_0)$$

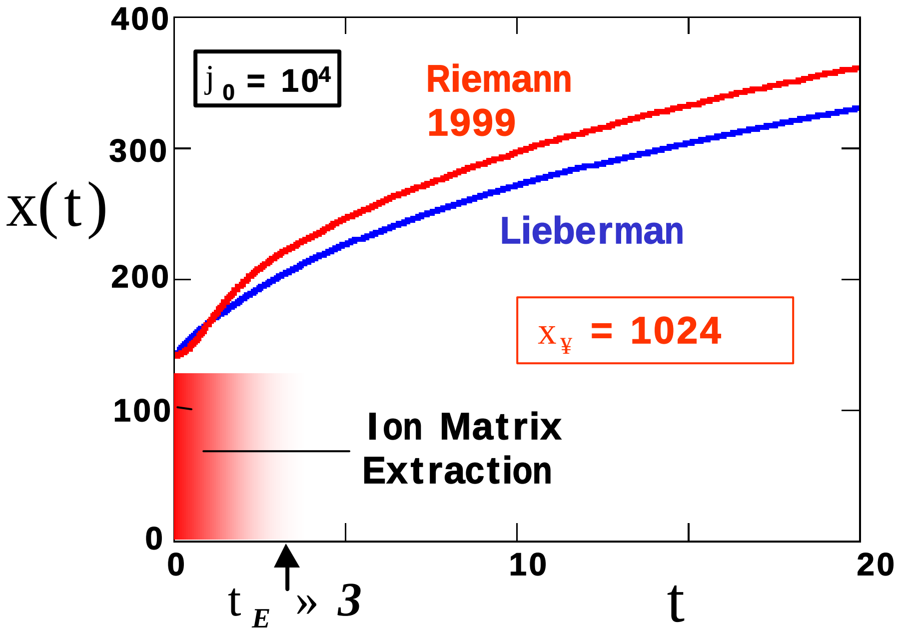
Matrix Extraction and Quasi-Static LC Phases Combined

- **Reduced quantities**

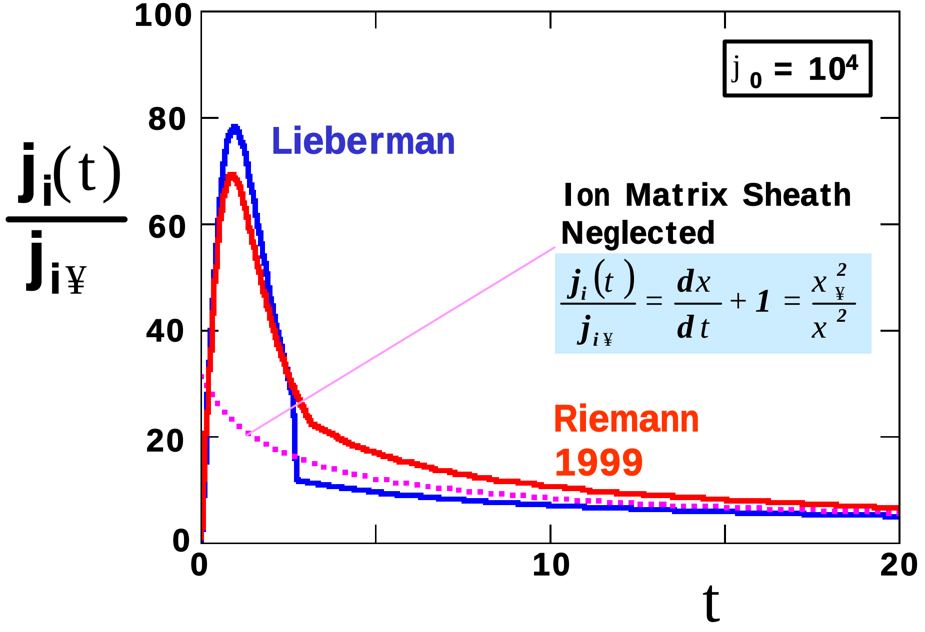
Sheath thickness $x = \frac{x_s}{l_D}$ **Time** $t = t\,w_{pi}$ **Voltage** $j_0 = \frac{eV_0}{kT_e} >> 1$

- **Infinitely short pulse rise time**

Sheath Expansion



Relative Ion Flux



Example: CH_4, above parameters, V_0 = 11 kV
$w_{pe} = 1.3 \cdot 10^{10}\ s^{-1}$; $w_{pi} = 7.6 \cdot 10^{7}\ s^{-1}$; $l_{Debye} = 3.5 \cdot 10^{-3}$ cm → x_s = 3.6 cm

Liebermann and Lichtenberg, loc.cit.

Riemann and Daube, JAP 86(1999)1202

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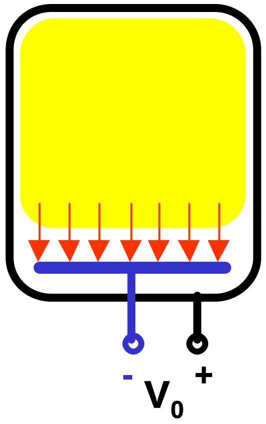
March 2003

Plasmas with High Ion Energy at Substrate/Target

- **DC plasma**

Plasma potential is slightly (some eV) above anode potential
Operation voltage ~ 100 V ... 1 kV
High ion energy ~ 100 eV ... 1 keV, monoenergetic w/o collisions

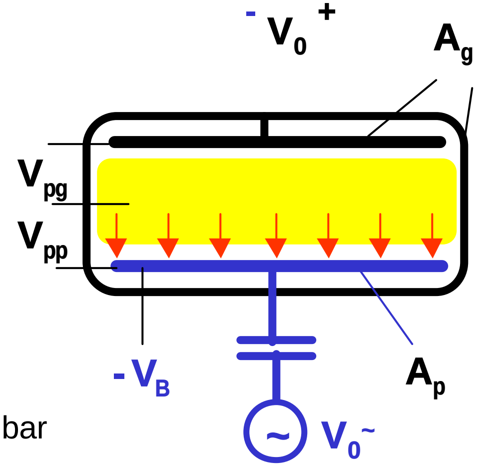


- **Capacitatively coupled RF plasma**

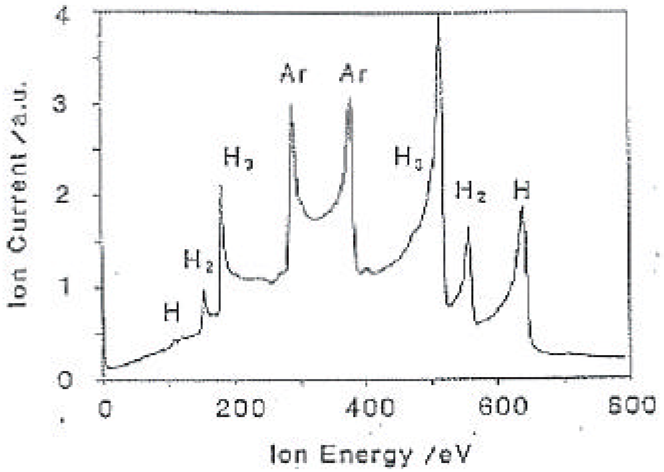
Operation frequency ~ 10 ... 100 MHz
Operation amplitude $V_0^{\sim}$ ~ 100 V ... 1 kV
Negative self-bias at powered electrode with $V_B \gg V_0^{\sim}$
Plasma potential adjusts between powered and grounded electrodes; $V_{pg}+V_{pp} = V_B$ according to areas

$$\frac{V_{pp}}{V_{pg}} = \left(\frac{A_g}{A_p}\right)^{2\ldots3}$$

High ion energy ~ 100 eV ... 1 keV



Double peaked ion energy distributions functions for $\omega_{RF} \gg \omega_{pi}$



$4\cdot10^{-3}$ mbar
Ar + H_2
Ar/H_2 = 0.4
13.56 MHz
V_0 = 465 V

Kuypers and Hopman, JAP 63(1988)1894

Plasmas with Low Ion Energy at Substrate/Target

- **Microwave plasma**

  Operation frequency 2.45 GHz
  Low ion energy ~ 10 eV ... 20 eV
  Narrow ion energy distribution (width few eV)

- **Inductively coupled RF plasma**

  Operation frequency ~ 10 ... 100 MHz
  Low ion energy ~ 10 eV ... 20 eV if purely inductive (often capacitive component!)
  Narrow ion energy distribution (width few eV)

- **Surface wave plasma**

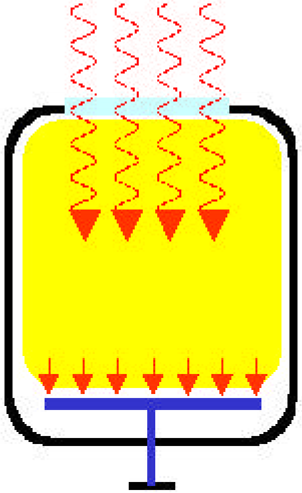
  Operation frequency 2.45 GHz
  Very low ion energy ~ 5 eV
  Narrow ion energy distribution (width few eV)

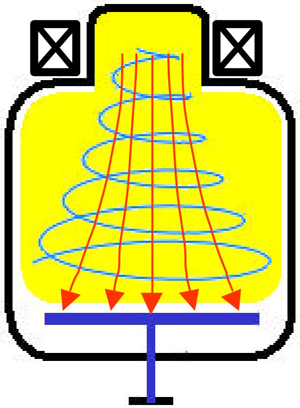
- **ECR plasma with divergent magnetic field**

  Operation frequency 2.45 GHz @ 87.5 mT
  Ambipolar ion acceleration due to electron drift
  Ion energy < ~ 50 eV
  Broader ion energy distribution (often bimodal)

- **Combination with DC or RF bias**

  Variable, well defined ion energy


Electrodeless discharges


ECR

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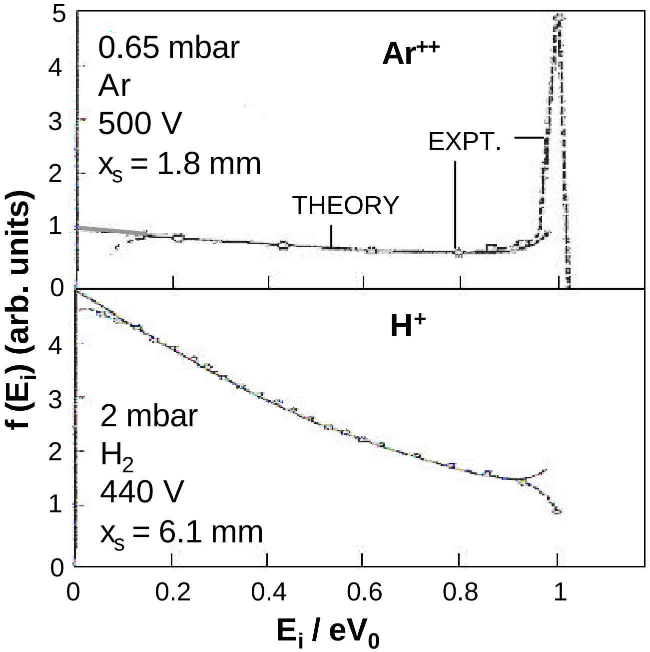
Collisional Sheaths $l_0 < x_s$

- **DC plasma**

Simplified model by Davis and Vanderslice
(Charge transfer collisions only)

$$f(E_i) = \frac{1}{eV_0}\,\frac{l_0}{x_s}\,\frac{1}{2\sqrt{1-E_i/eV_0}} \times \exp\left[-\frac{x_s}{l_0}\left(1-\sqrt{1-E_i/eV_0}\right)\right]$$

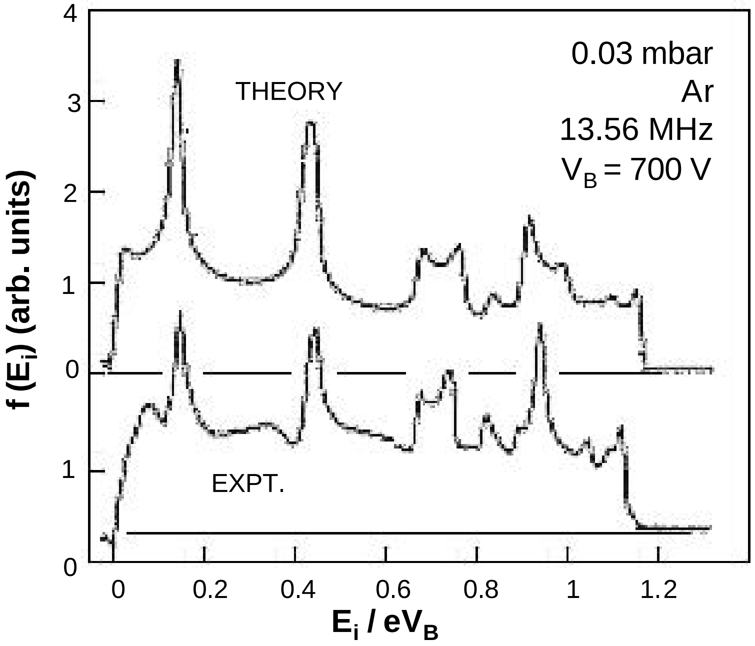
+ possibly remaining full-energy peak



Davis and Vanderslice, PR 131(1963)219

- **RF plasma**

Multiple peak ion energy distribution due to correlated charge-exchange collisions and oscillatory motion in sheath



Wild and Koidl, APL 54(1989)505

Surface Processes

Reading

M. Nastasi, J.W. Mayer and J.K. Hirvonen, *Ion Solid Interactions: Fundamentals and Applications*. Cambridge, U.K.: Cambridge University Press, 1996.

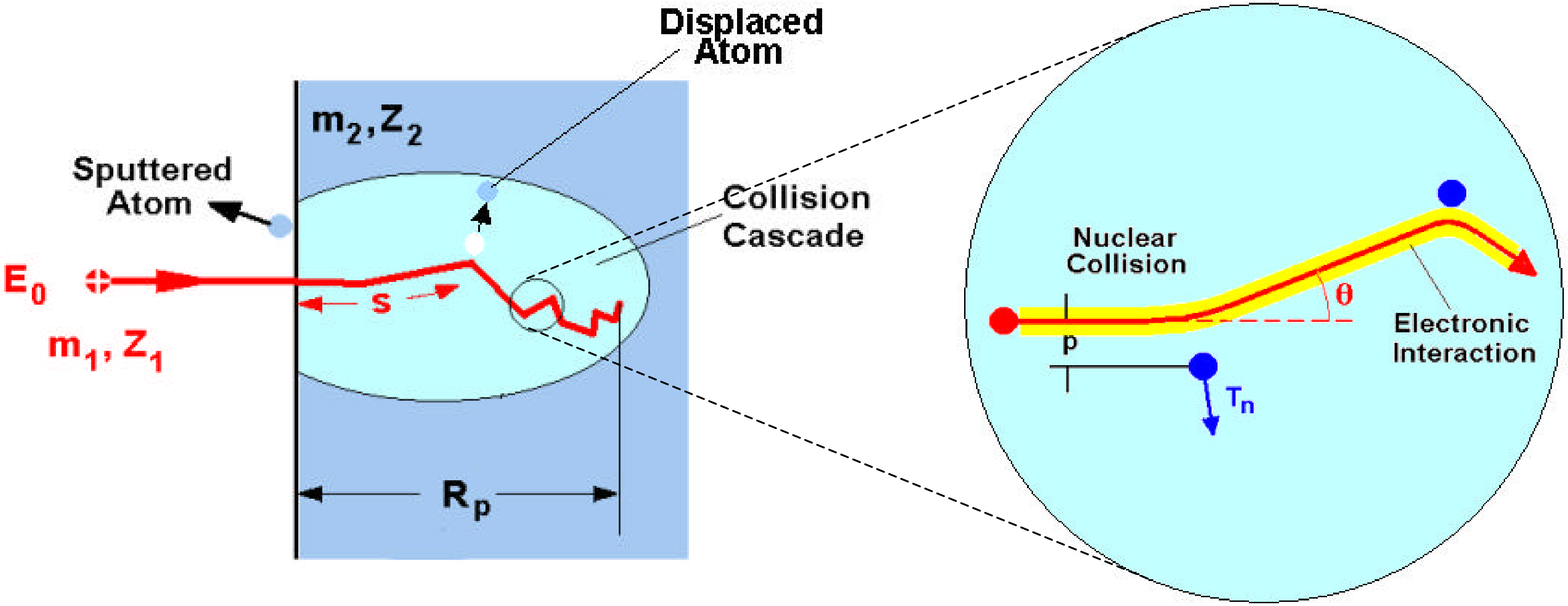
A.Anders (Ed.), *Handbook of Plasma Immersion Ion Implantation and Deposition.* New York, John Wiley & Sons, 2000.
(Chapter 3 by M. Nastasi, W. Möller and K. Ensinger)

H.Frey (Ed.), *Vakuumbeschichtung 1.* Düsseldorf: VDI – Verlag, 1995.
(Chapter 3 by W. Möller)

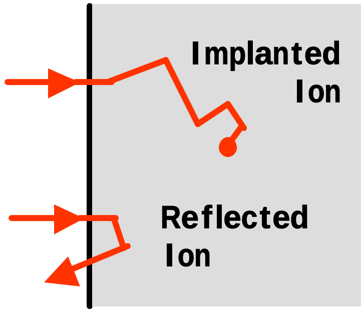
R. Behrisch (Ed.), *Sputtering by Particle Bombardment I.* Berlin: Springer, 1981.

W. Möller, *Plasma and Surface Modelling of the Deposition of Hydrogenated Carbon Films from Low-Pressure Plasmas,* Appl.Phys. A56(1993)527

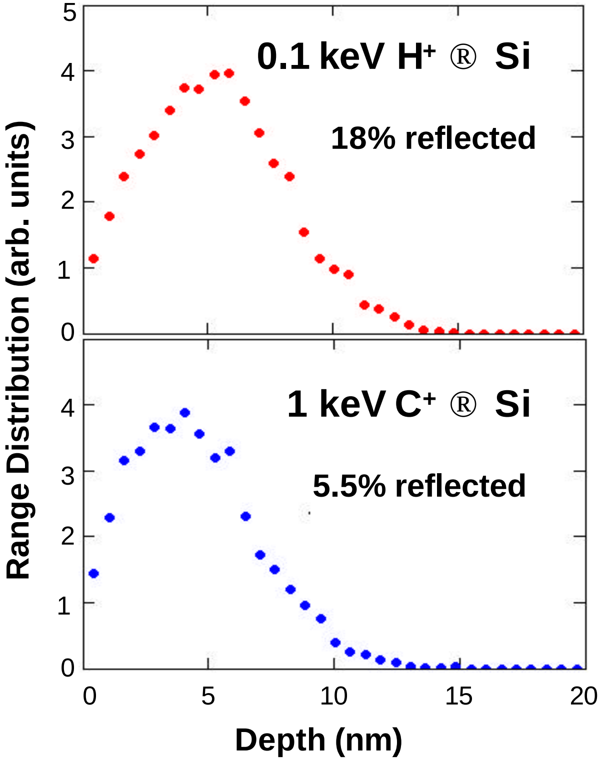
Ion-Surface Interaction



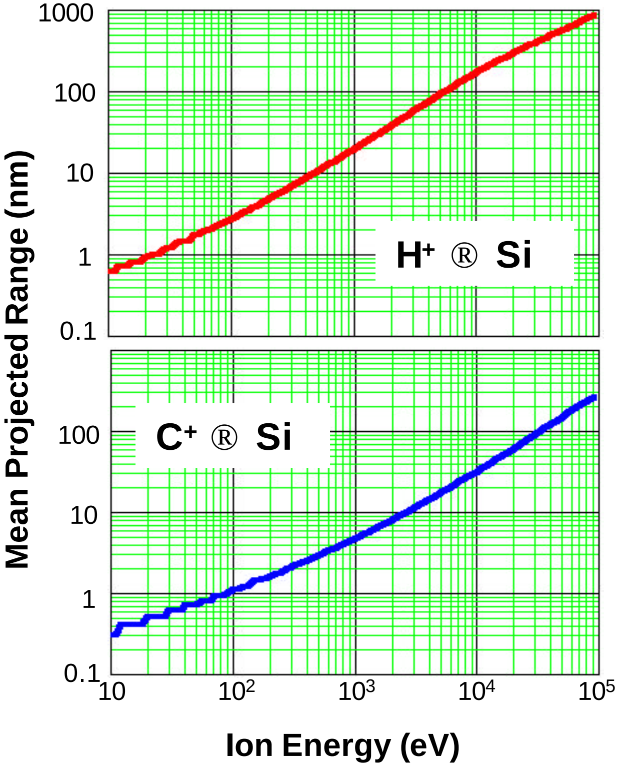
Ion Ranges and Reflection



TRIM Computer Simulation

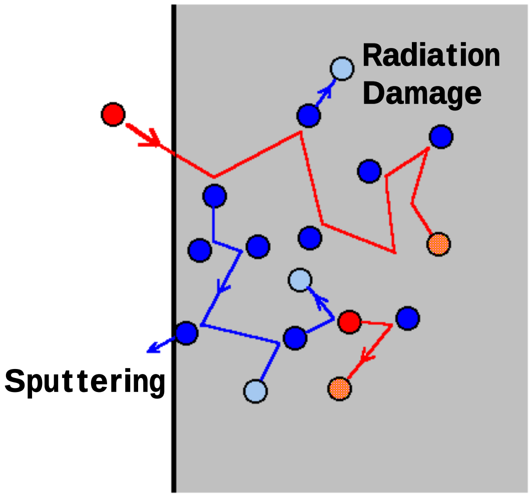


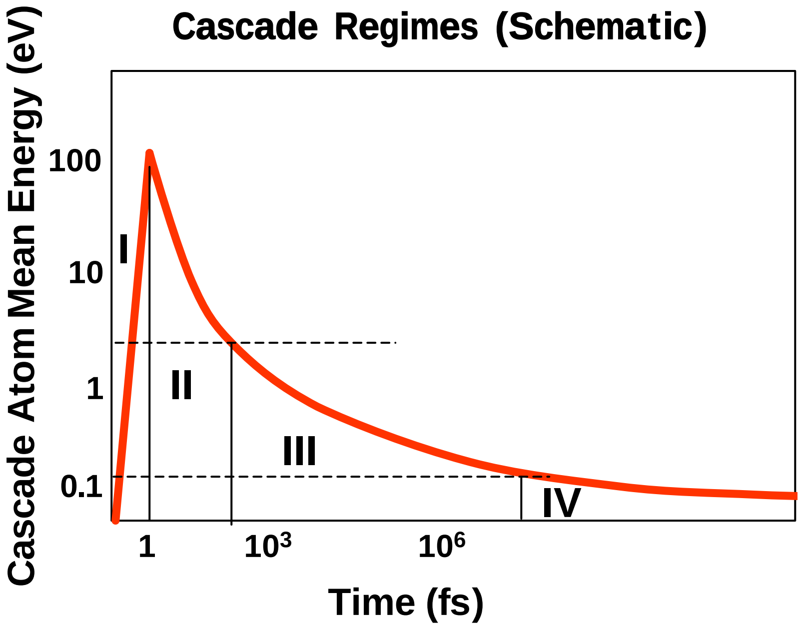
Analytical Range Algorithm



http://www.srim.org (J.F. Ziegler)

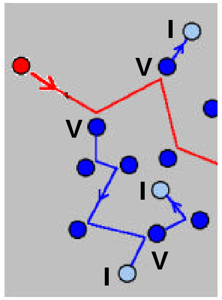
Collision Cascades





Regime		Time	Energy Range	Processes	Computer Simulation
I	Ion slowing down	~ fs	£ Incident energy	Sputtering (> ~ 3eV) Damage (> ~ 20 eV)	Binary Collision Approximation (BCA) (TRIM)
II	Collisional	~ fs...ps	~ 100 eV ... 3 eV		
III	Hyperthermal	~ ps...10 ns	~ 3 eV ... 0.1 eV	Thermal spike Low-activation reordering Hot chemistry	Molecular Dynamics (MD)
IV	Thermal	> ~ 10 ns	< 0.1 eV	Diffusion Chemical reactions	Kinetic Monte Carlo (KMC)

Radiation Damage



Generation of interstitial (I) – vacancy (V) pairs ("Frenkel pairs") requires minimum separation of I and V, corresponding to a damage threshold energy of the recoil atom, U_d.

Depending on material, $U_d = 15...80$ eV

Reasonable approximation for mean number of Frenkel pairs per incident ion

$$N_{FP}(E_i) » \begin{cases} 0 & \text{if} \quad E_i < U_d \\ \dfrac{E_i}{2U_d} & \text{else} \end{cases}$$

(Kinchin-Pease model)

Unit for Frenkel pair (or vacancy) concentration is dpa (displacements per atom)

- **Frenkel pair concentration is limited at high ion fluence**

Max. few % in pure metals
Amorphization achievable in,
e.g., semiconductors at R.T.

In simplest model of amorphization, critical fluence is given by an average vacancy concentration of 1 dpa within the double mean projected ion range

$$F_{amorph}(E_i) » 2\frac{R_p(E_i) \cdot n \cdot E_d}{E_i}$$

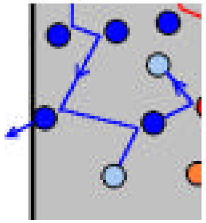
- **Point defects (I and V) become mobile at elevated temperature**

I in metals: @ few 10 K
V in metals: @ few 100 K
I,V in semiconductors: @ few 100 K

⇩

Annihilation, clustering ...
depending on material few 100 K

Collisional or "Physical" Sputtering



Sputtered atom has to overcome surface binding energy U_0

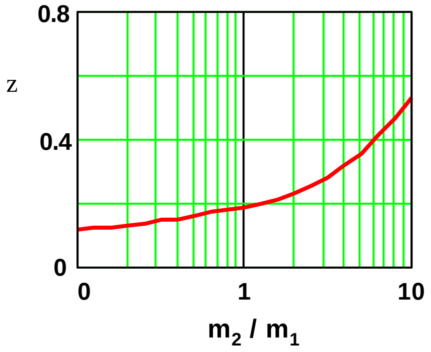
Good approximation for monoatomic surfaces $U_0 = \Delta H^{sublim}$

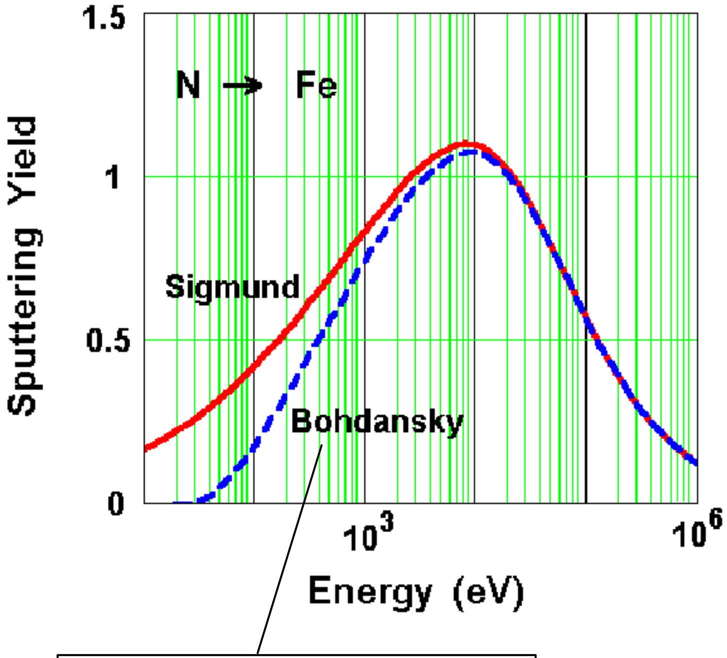
Sputtering Yield $Y_s = \frac{Nr.\ of\ Sputtered\ Atoms}{Nr.\ of\ Incident\ Ions}$

$$Y_s(E_i) = \frac{4.2 \cdot 10^{14} cm^2}{U_0} \cdot \alpha \left(\frac{m_2}{m_1}\right) \cdot S_n(E_i)$$

(Sigmund) E_i Incident Ion Energy

α Momentum reversal factor





Bohdansky: Correction for threshold effects

- Good results from BCA computer simulation (TRIM)

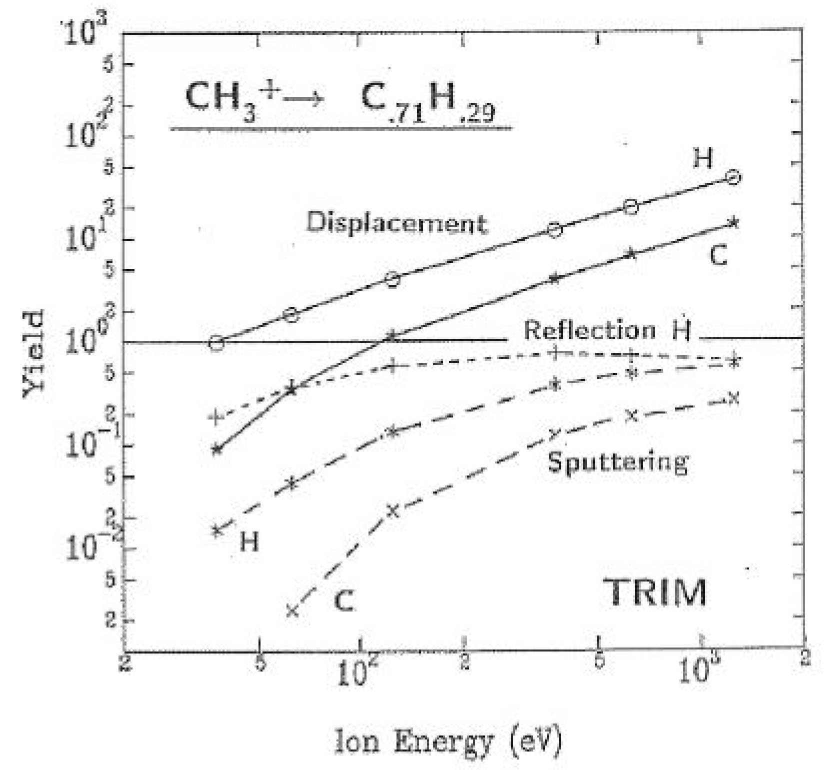
Example: Ion Collisional Effects from CH_4 Plasma

CH_3^+ taken asrepresentative for ions
Amorphous hydrogenated carbon surface with H/C = 0.4

Molecule assumed to split a into atoms k (k = 1...4) at first surface collision, with (energy and momentum conservation)

$$E_{ik} \sim m_k \qquad \sum_k E_{ik} = E_i$$

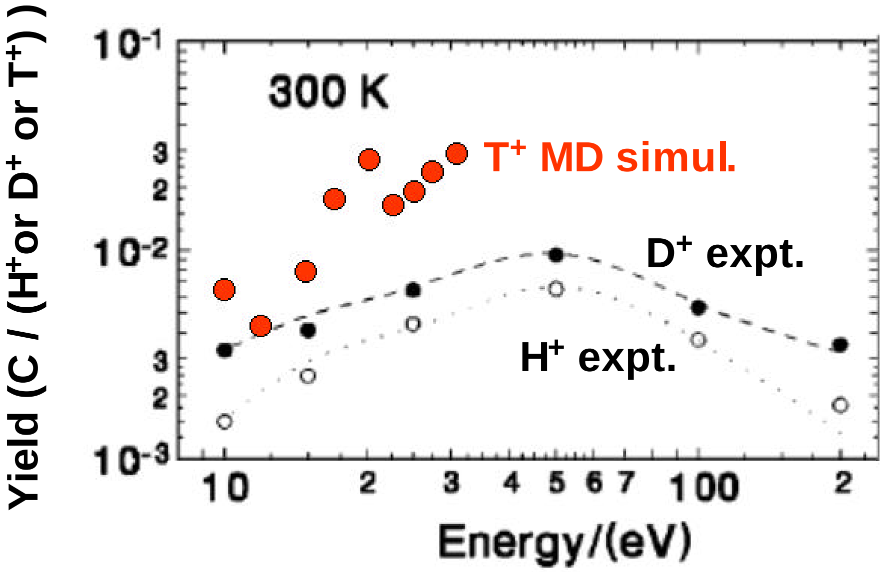
resulting in
$E_{i,C} = 12/15\ E_i$, $E_{i,H} = 1/15\ E_i$



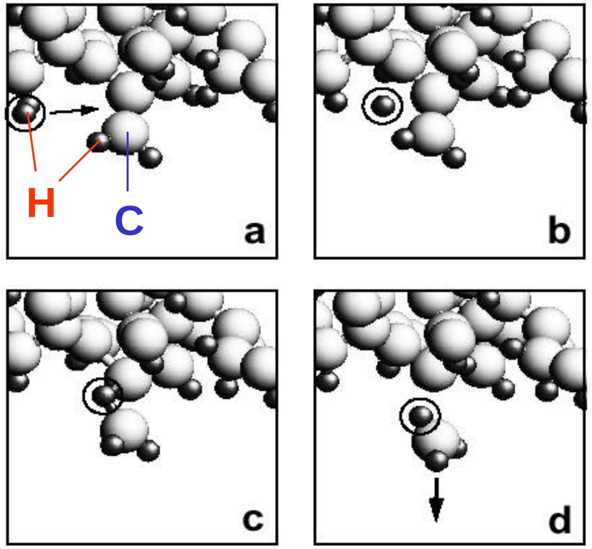
W. Möller, APA 56(1993)527

“Chemical” Sputtering

- **Hot chemical reactions leading to surface erosion**
- **Threshold energy significantly lower than for physical sputtering**
- **Best investigated for H^+ ® C:H**



Mechanism identified by molecular dynamics computer simulation

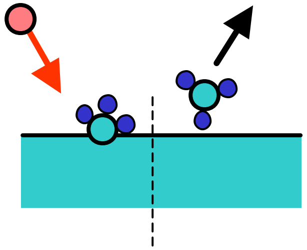


Mech et al., JAP 84(1998)1655

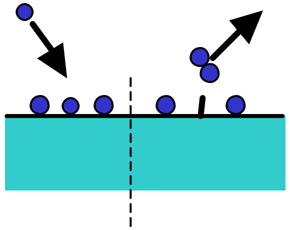
Salonen et al., Europhys.Lett. 52(2000)504

Surface (Hot) Chemistry (Schematic Examples)

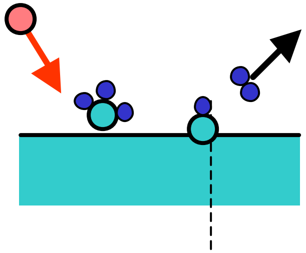
- Ion-induced desorption by physical or chemical sputtering (Bond breaking)



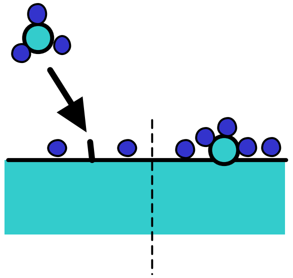
- Hydrogen abstraction



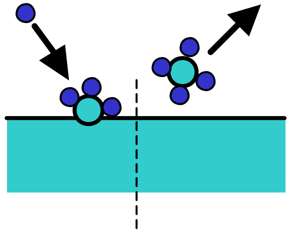
- Ion-induced bond formation with physisorbed radicals ("Ion stitching")



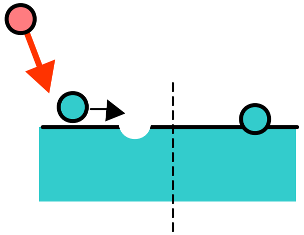
- Radical insertion



- Surface reactions with radicals



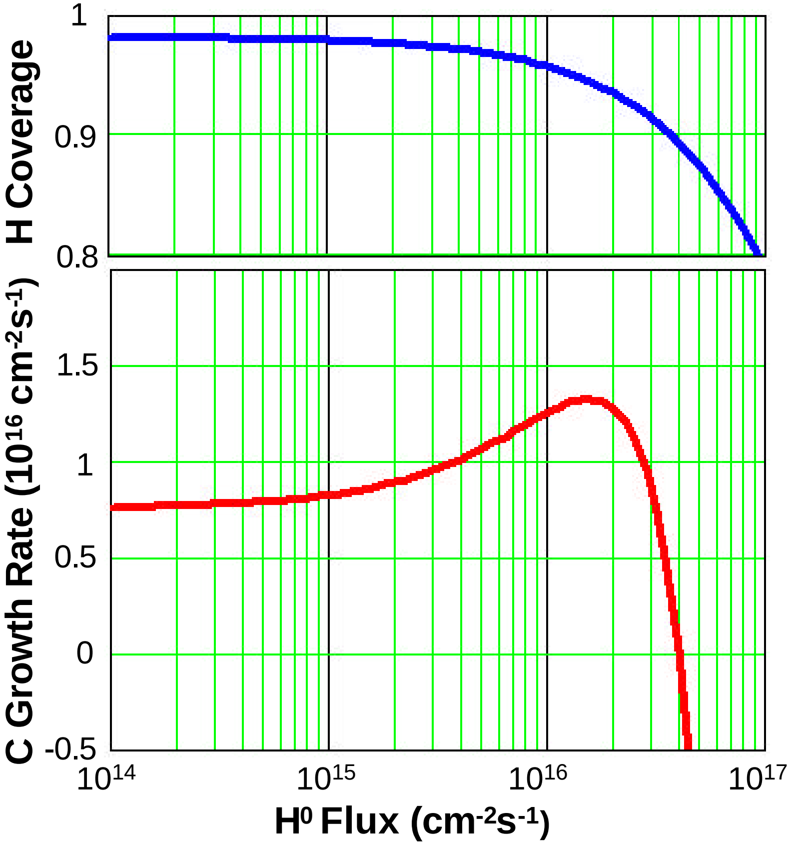
- Ion-induced surface reaction by enhanced surface mobility



Example of Surface Chemistry Modeling

Growth of C:H films from a methane plasma

$j_{CH3} = 4\cdot10^{17}$ cm^{-2}s^{-1}; $j_i = 7.8\cdot10^{15}$ cm^{-2}s^{-1}
$\sigma_{dam,abs,ins} = \alpha_0^{-1} = 7\cdot10^{-16}$ cm^2; $\sigma_{ree} = 10\,\alpha_0^{-1} = 7\cdot10^{-15}$ cm^2



Assumptions:

Two different surface sites

activated: coverage q_A
passive (hydrogen terminated): coverage q_H

$$q_A + q_H = 1$$

Activation by

Ion-induced damage: Flux j_i, cross section s_{dam}
Hydrogen abstraction: Flux j_H, cross section s_{abs}

Growth / Erosion by

Insertion of CH_3 radicals: Flux j_{CH3}, cross section s_{ins}
Hydrogen reetching: Flux j_H, cross section s_{ree}

Balance equation

$$0 = \frac{dq_A}{dt} = s_{dam}\, j_i (1 - q_A) - s_{abs}\, j_H q_H - s_{ins}\, j_{CH_3} q_A$$

Growth rate

$$j_g = (s_{ins}\, j_{CH_3} - s_{ree}\, j_H) q_A a_0$$

a_0 **Carbon surface areal density**

Ion Bombardment and Thin Film Deposition

Reading

R.F. Bunshah, G.E. McGuire and S.M. Rossnagel (Eds.), *Handbook of Deposition Technologies for Films and Coatings.* Park Ridge, N.J.: Noyes, 1994.

J.E. Greene et al. in: *Plasma Surface Interactions and Processing of Materials*, NATO ASI Series E, Vol. 176, O. Auciello, A. Gras-Marti, J.A. Valles-Abarca and D.L. Flamm (Eds.), 1990.

J.W. Rabalais (Ed.), *Low Energy Ion-Surface Interactions.* Chichester: John Wiley & Sons, 1994.
(Chapter 8 by N. Herbots et al.; Chapter 9 by D. Marton; Chapter 10 by J. Rudnick and R. Bruinsma)

A.Anders (Ed.), *Handbook of Plasma Immersion Ion Implantation and Deposition.* New York, John Wiley & Sons, 2000.
(Chapter 3 by M. Nastasi, W. Möller and K. Ensinger)

H.Frey (Ed.), *Vakuumbeschichtung 1.* Düsseldorf: VDI – Verlag, 1995.
(Chapter 3 by W. Möller)

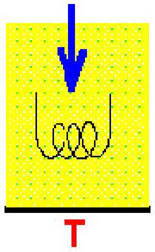
Mühlleithen
March 2003

FORSCHUNGSZENTRUM ROSSENDORF
Institute of Ion Beam Physics and Materials Research

Plasma- and Ion-Based Deposition of Thin Films

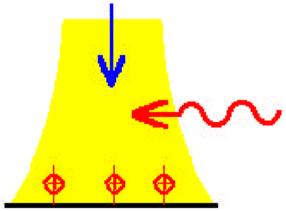
CVD

Chemical Vapour Deposition



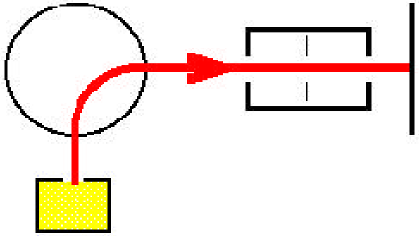
PECVD

Plasma Enhanced Chemical Vapour Deposition



IBD

Ion Beam Deposition



Characteristic Ion Energies

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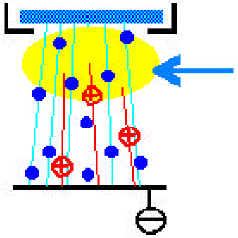
0.01... 1 keV

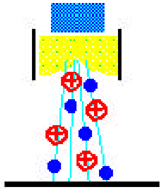
0.01... 10 keV

Magnetron Sputtering



0.01 keV unbiased
... 1 keV biased

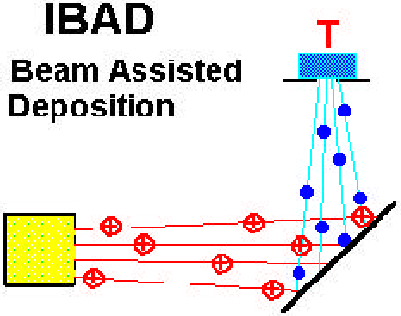
Arc Evaporation



0.01 ... 0.1 keV

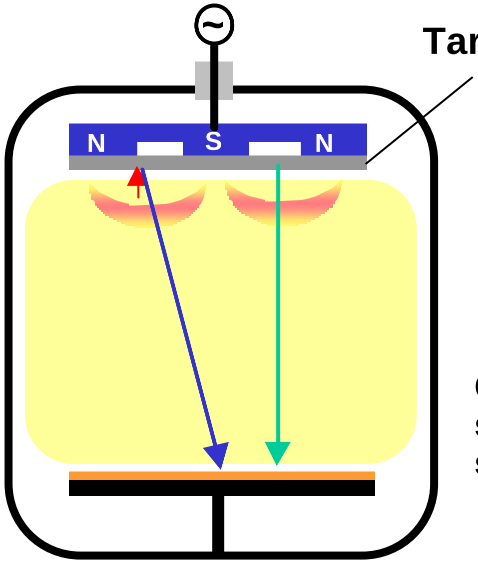
IBAD

Ion Beam Assisted Deposition



0.1... 10 keV

(Unwanted) High-Energy Bombardment: Magnetron Sputtering



Target at negative DC
or RF Bias
(several 100 V)

Reflected Neutrals

by reflection and
neutralisation of
sputtering ions

Negative Ions

Generated at target
surface by, e.g.,
sputtering

Radiation Damage

Deteriorates properties of
high-grade electronic or
optical films

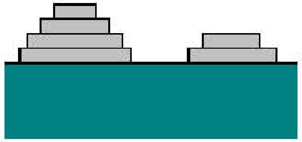
- **Diagnostics ?** (Mass Spectrometry ???, ...???)
- **Influence of Target Condition ?**
- **Control ?** (Plasma Conditions, Additives, ...???)

Thin Film Growth and Ion Bombardment

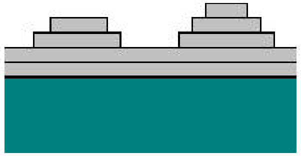
Growth Modes

Layer-by-Layer (Franck - van der Merwe)

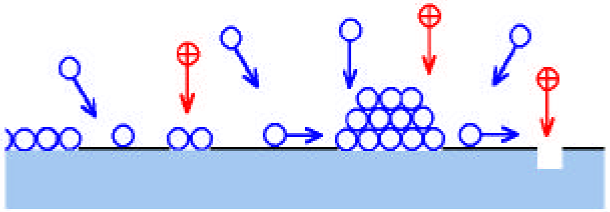
Island (Vollmer - Weber)



Mixed (Stranski - Krastanov)



- **Surface Effects**

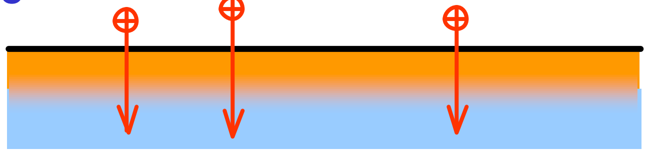


Enhanced Surface Mobility
Dissolution of Islands
Surface Defects
Surface Activation

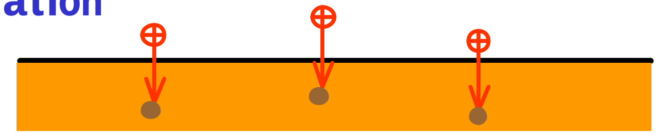
→

Homogeneous Nucleation
Early Growth
Morphology
Compound Formation

- **Interface Mixing**



- **Subplantation**



Growth Below Surface

→

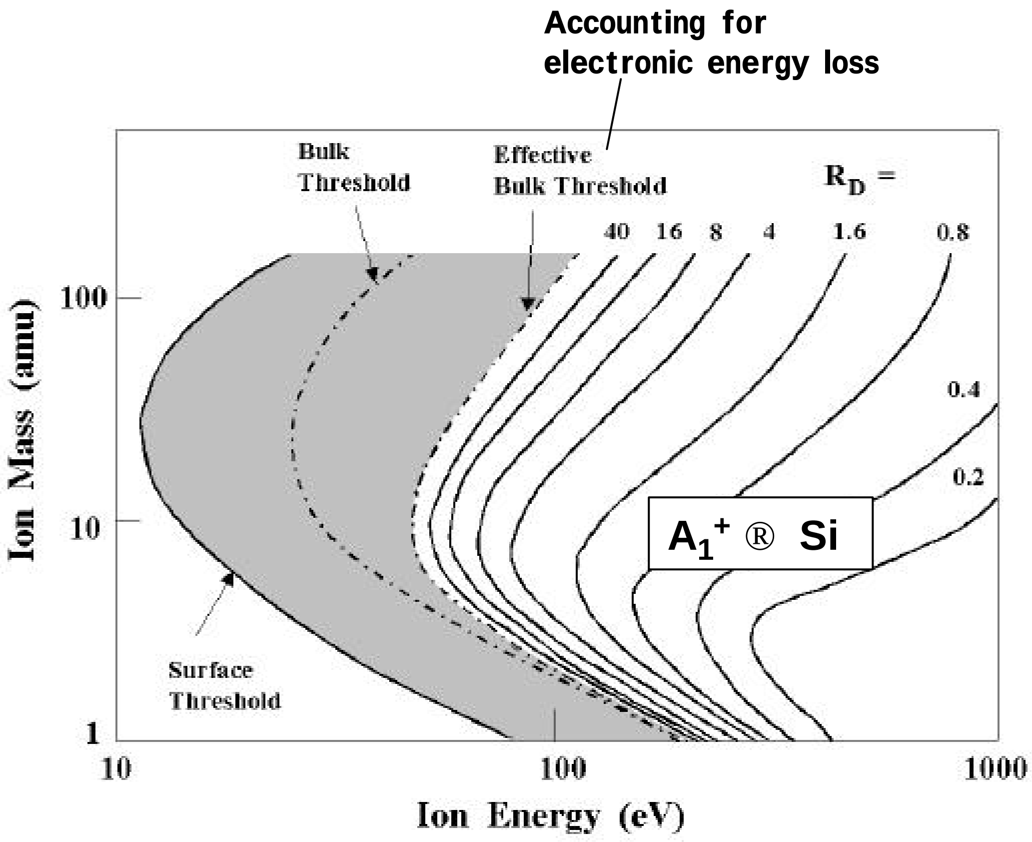
Structure Accomodation
Stress Formation
Film Densification

Damage during Ion-Assisted Deposition

- **Bulk damage to be avoided**
- **Moderate surface damage desirable: Surface Mobility!**
- **Damage threshold at surface smaller than in bulk**
  (Nuclear Collisions)

$$U_d^{surf} \approx 0.2 \ldots 0.3 \times U_d^{bulk}$$

- **Favourable Regime of Ion Energy (~50 eV)**

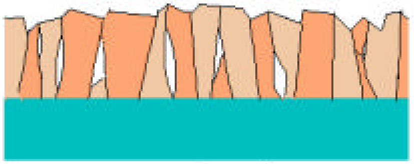


Accounting for electronic energy loss

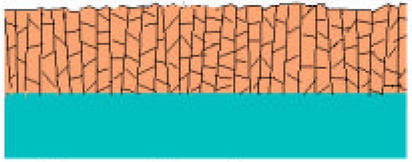
J.Y Tsao et al., NIMB 39(1989)72

Film Morphology

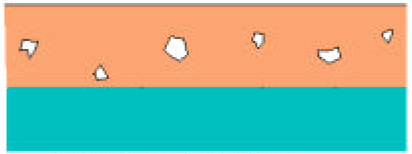
Ion Bombardment ↓



coarse-grain columnar, porous

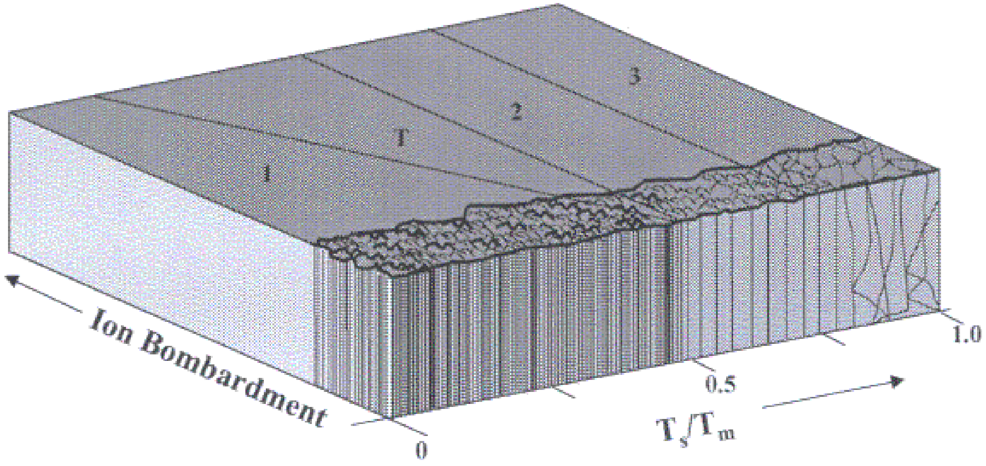


fine-grain columnar, dense



nanocrystalline, porous

Growth zones according to Thornton



Zone	Morphology	Mechanisms
1	porous, rough, nanocrystalline	no surface diffusion
T	rough, grain growth	slow surface diffusion
2	recrystallization, columnar	fast surface diffusion
3	large grain crystallization	bulk diffusion

⇨ Ion bombardment replaces substrate temperature (zones 1 & T)

J.A. Thornton, JVST 11(1974)666

Film Densification: Computer Simulation

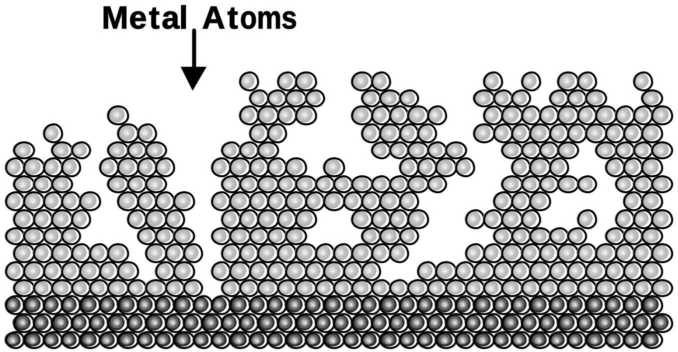
Deposition of a metal assisted by argon ions

2D molecular dynamics simulation

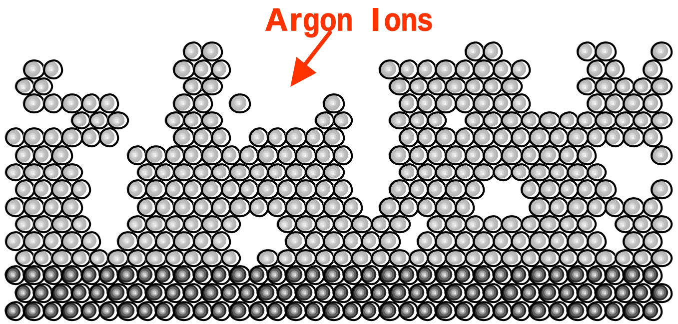
Lennard-Jones potential

K.-H. Müller, JAP 62(1987)1796

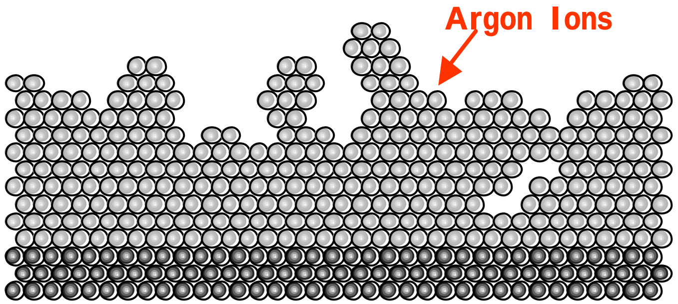
Metal Atoms Only



50 eV Ar^+
$Ar^+/Me = 0.04$

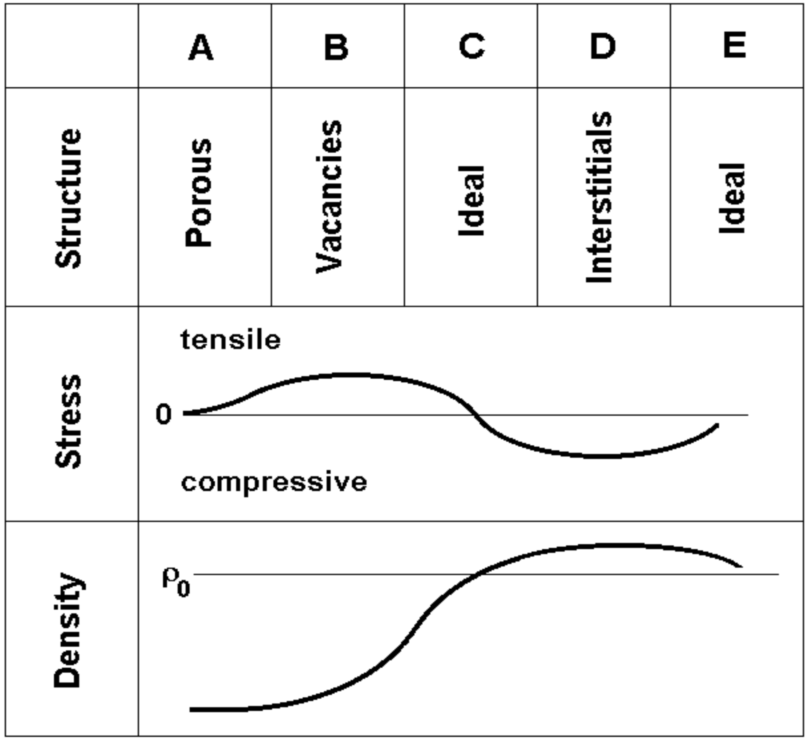


50 eV Ar^+
$Ar^+/Me = 0.16$



Density, Stress and Morphology

(Qualitative Diagram)

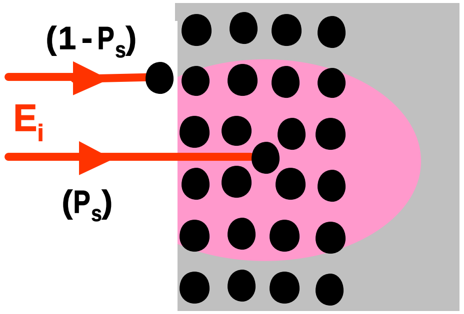


	A	B	C	D	E
Structure	Porous	Vacancies	Ideal	Interstitials	Ideal

Ion Bombardment

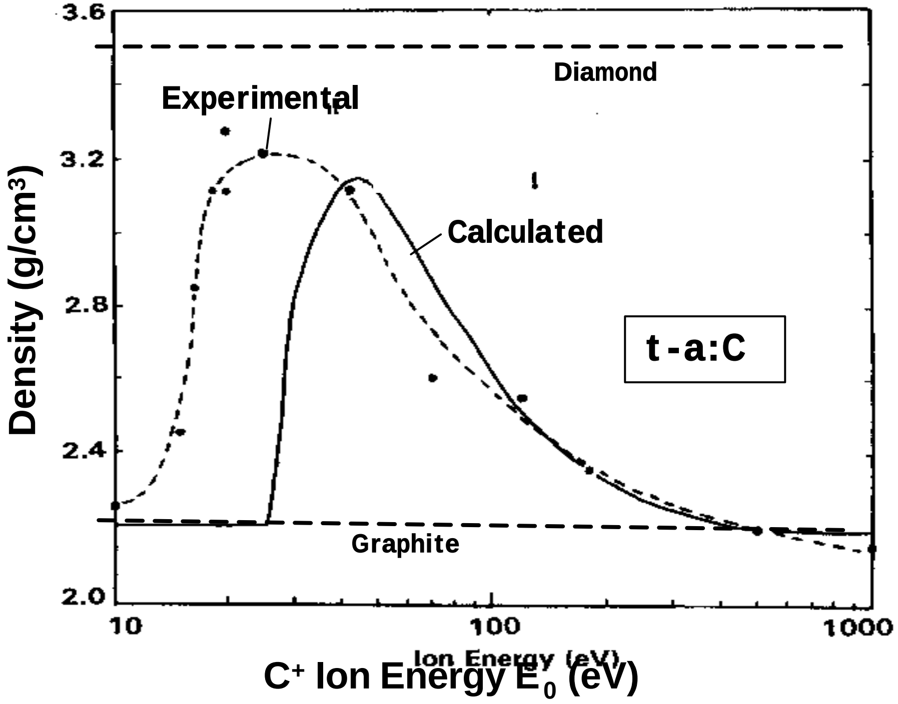
(Ion Energy and/or Ion-to-Neutral Ratio)

Subplantation Model (Ion Beam Deposition)



① Densification by ion implantation

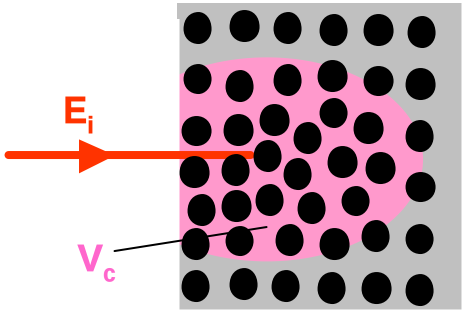
② Relaxation by hyperthermal cascade



"Subplantation" of fraction P_s of incident flux, yielding interstitial atoms and dense phase. Remaining fraction is deposited at surface, as normal lattice atoms.

J. Robertson, Phil.Trans.R.Soc.Ldn A342(1993)277

Cylindrical Spike Model (Ion Beam Deposition)



- Dense phase formation by rearrangement in hyperthermal cascade

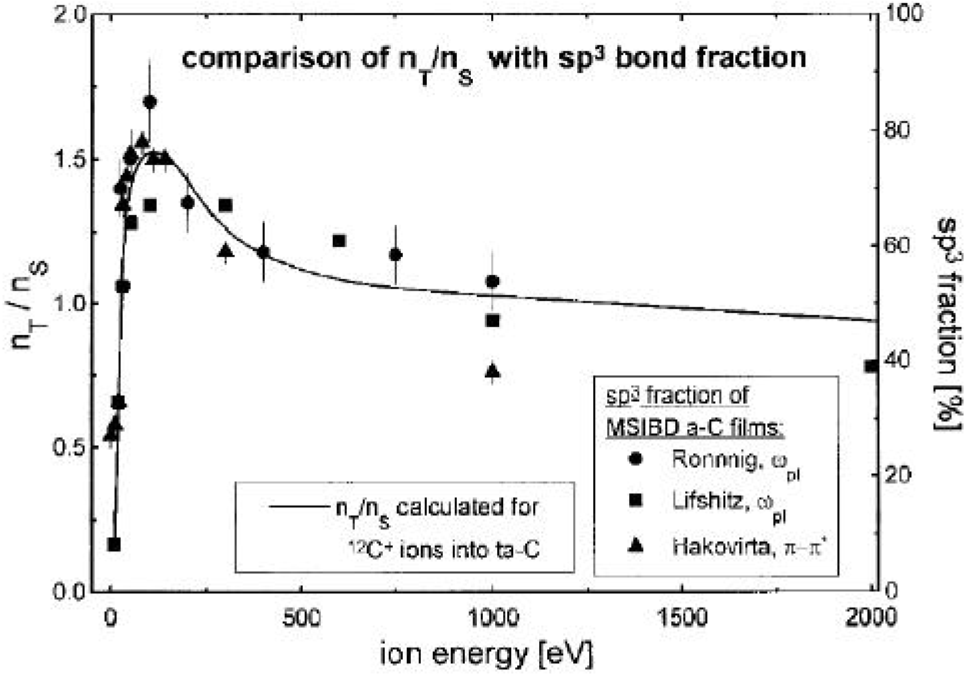
Comparison of the number of rearrangements, n_T, to the total number of atoms in the thermal spike, n_S

$$\frac{n_T}{n_S} \approx \frac{0.014\ nm}{R_p(E_i)} \left(\frac{Q(E_i)}{U_r} \right)^2$$

U_r Activation energy of rearrangement

$Q(E_i)$ Fraction of incident energy which is not deposited electronically nor into damage ("phonon" fraction from TRIM computer simulation)

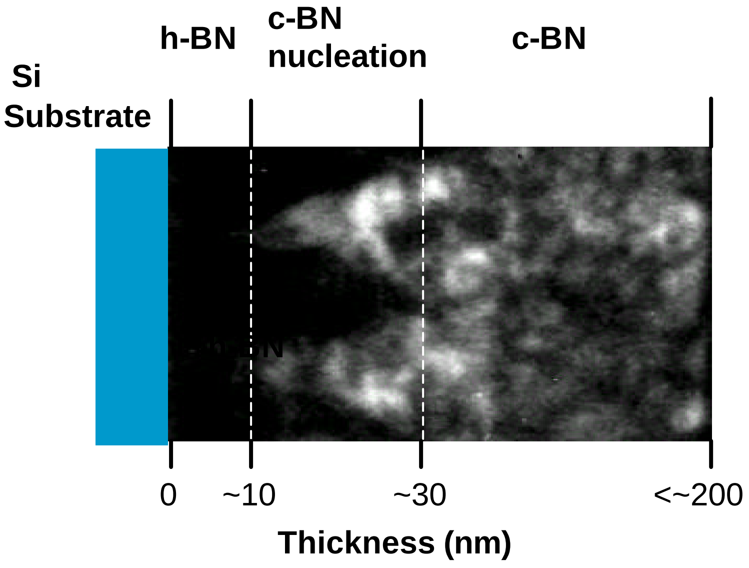
t-a:C by mass-selected ion beam deposition



H. Hofsäss et al., APA 66(1998)153

Stress Release in c-BN

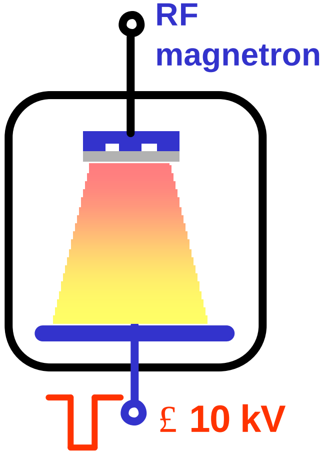
Conventional c-BN deposition
e.g., IBAD @ 340 ^{0}C



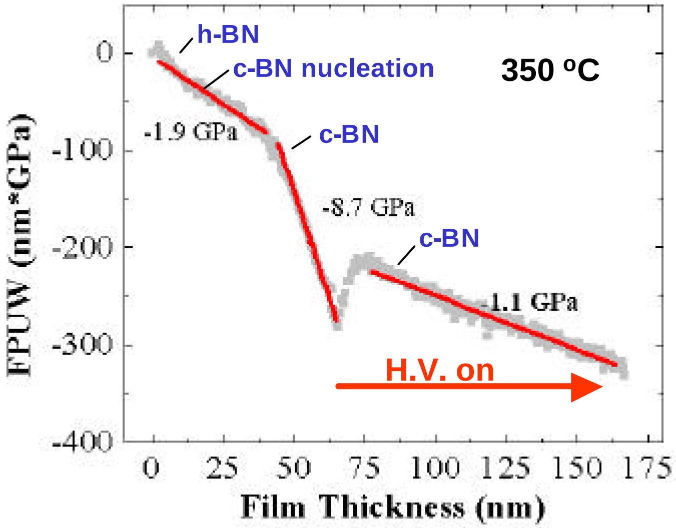
- **Max. c-BN thickness limited by excessive intrinsic stress**
(compressive; ~ 10 Gpa)

W. Fukarek, JVST A19(2001)2017

PIII assisted reactive magnetron sputtering



Real-time in-situ stress measurement



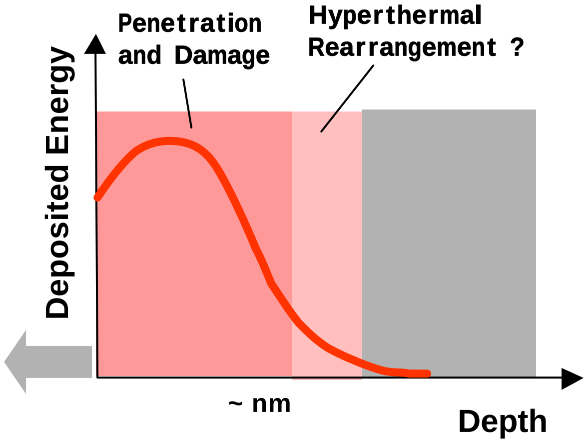
- **Significant release of stress**

B. Abendroth and W. Möller, recent results

Ion-Assisted Thin Film Growth: Open Questions

- **Where does the film grow ?**

  (Form its Final Structure ?)



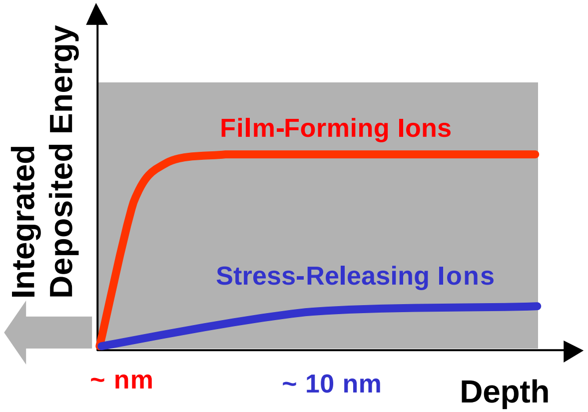
Depth-Dependent Modelling and Simulation Required

- **Stress Formation**

  Correlated with Structure Formation

- **Stress Release**

  Example c-BN



- **Mechanisms of Texture Formation, Crystallization,...**