Characterization and *erosion* of metal-containing carbon layers

Martin Balden

Max-Planck-Institut für Plasmaphysik, EURATOM Association, D-85748 Garching, Germany
Materials Research Division (MF)

Outline

Introduction

- *Importance of mixed layers*
- *Why are we interested in metal-containing amorphous carbon layers (a-C:Me)?*

Characterization

- *Which material systems are investigated?*
- *How are specimens produced?*
- *Which characterization techniques are applied to obtain which material property?*

Chemical erosion by hydrogen impact

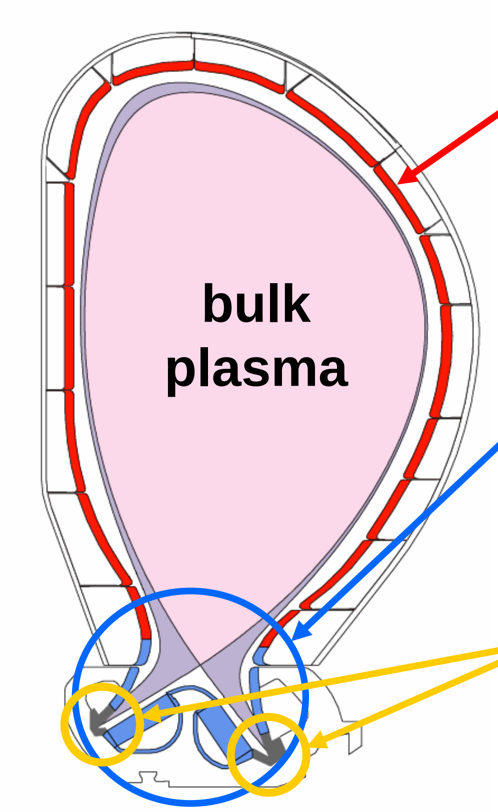
- *Total erosion yield of carbon: IBA*
- *Chemical erosion yield (CD_4): QMS*

Conclusion

Introduction

SEM

Plasma-facing materials: ITER design (Mix)



first wall: Be (low Z, O getter)

divertor wall: W (low erosion)

target plates: Carbon (CFC)
- **+ thermal shock resistance**
- **- chemical erosion**
- **- tritium inventory**

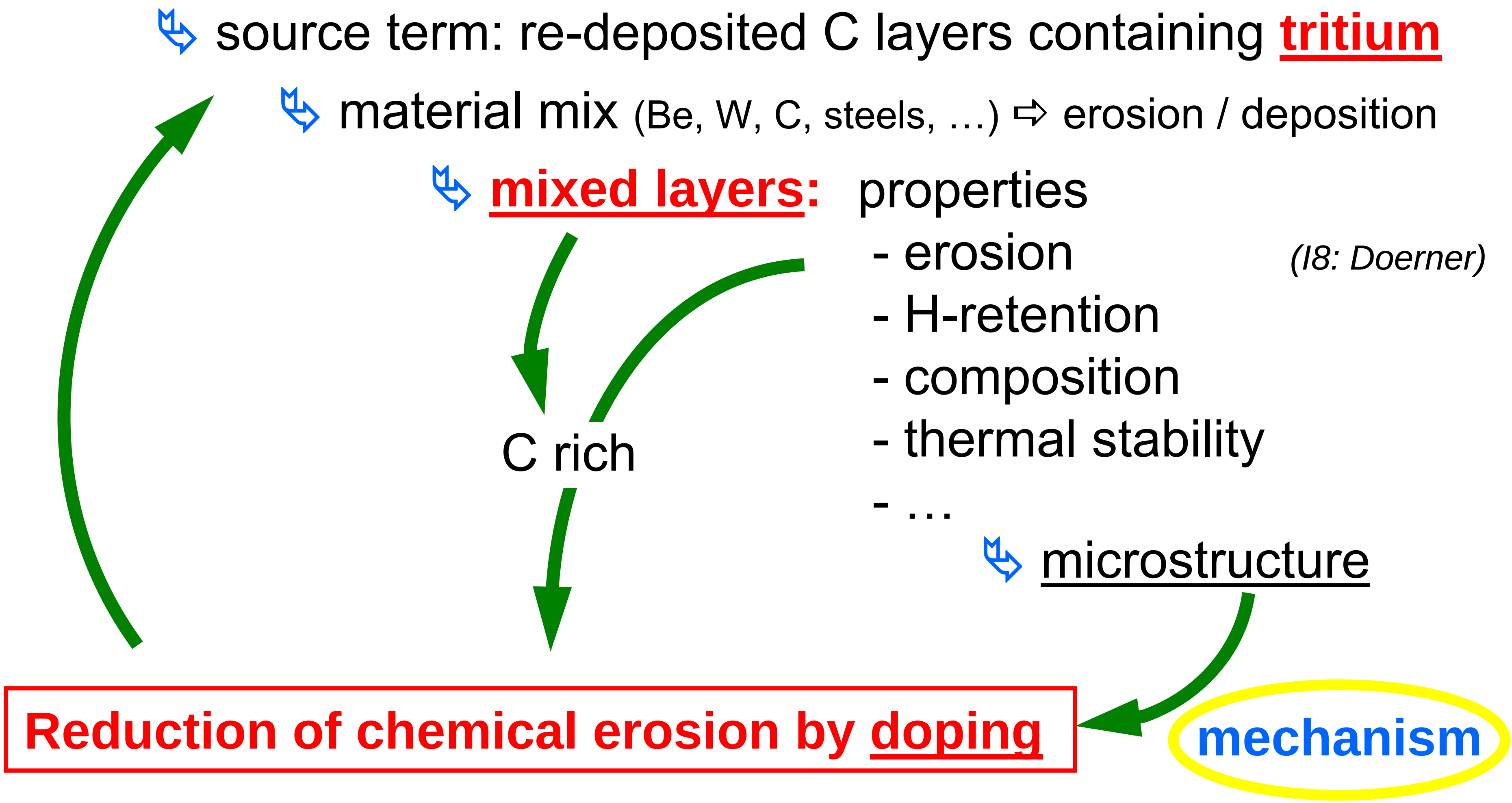
I3: Counsell

JET: ITER-like wall project

I10-13: Matthews, Hirai, Neu, Lungu, P06, P50-52

Introduction: Mixed materials & doping

<u>Chemical erosion of carbon by hydrogen</u>



↳ source term: re-deposited C layers containing **<u>tritium</u>**

↳ material mix (Be, W, C, steels, …) ⇨ erosion / deposition

↳ **<u>mixed layers</u>:** properties

- erosion (I8: Doerner)
- H-retention
- composition
- thermal stability
- …

↳ <u>microstructure</u>

C rich

Reduction of chemical erosion by <u>doping</u>

mechanism

Introduction: Metal-containing carbon films

- to simulate mixed layers
  - ↳ magnetron sputtered metal-containing carbon films
- well characterized <u>model materials</u>
  - ↳ **laboratory erosion studies on a-C:Me films**
    - ↳ **focused on W + C** (additional: Ti, V, Zr)

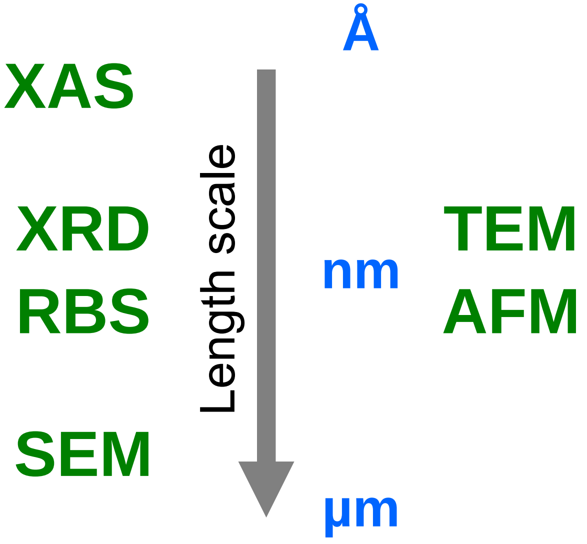
P30 Galilea

Introduction: Investigation strategy

Investigation of mixed layers

composition, distribution in depth, lateral homogeneity, impurities, crystallinity, chemical state, film morphology

- characterization on
  - - atomic level
  - - nanometer scale
  - - micrometer scale



- **chemical erosion**
  - **energy & mass-separated hydrogen ion beam**:

+ total erosion yield: **MeV ion beam analysis** (weight loss; in-situ)

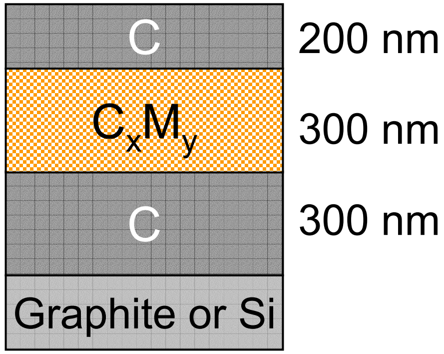
+ chemical erosion yield: **mass spectrometry**

Outline

Production
and
Characterization

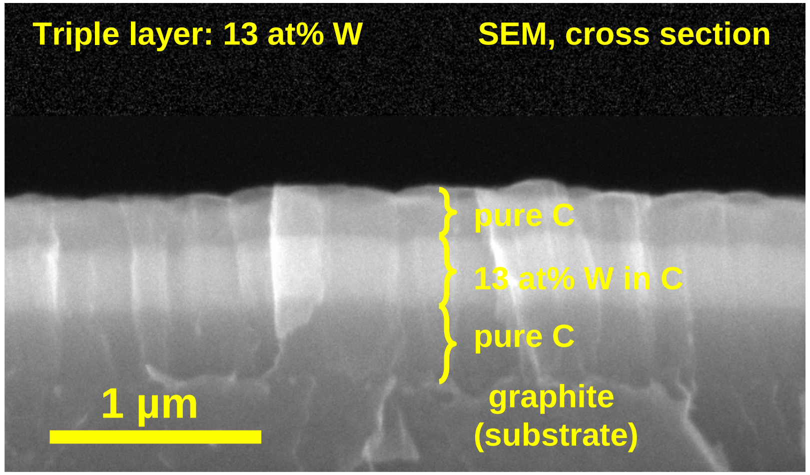
Production of a-C:Me layers

- metal-doped amorphous carbon layers:
  - **magnetron sputter deposition** dual source, 300 K
  - **single** and **triple** layers on graphite or Si
    - ↳ erosion 0.2-2 µm
    - ↳ thermal treatment, diffusion
    - ↳ no surface-substrate influence



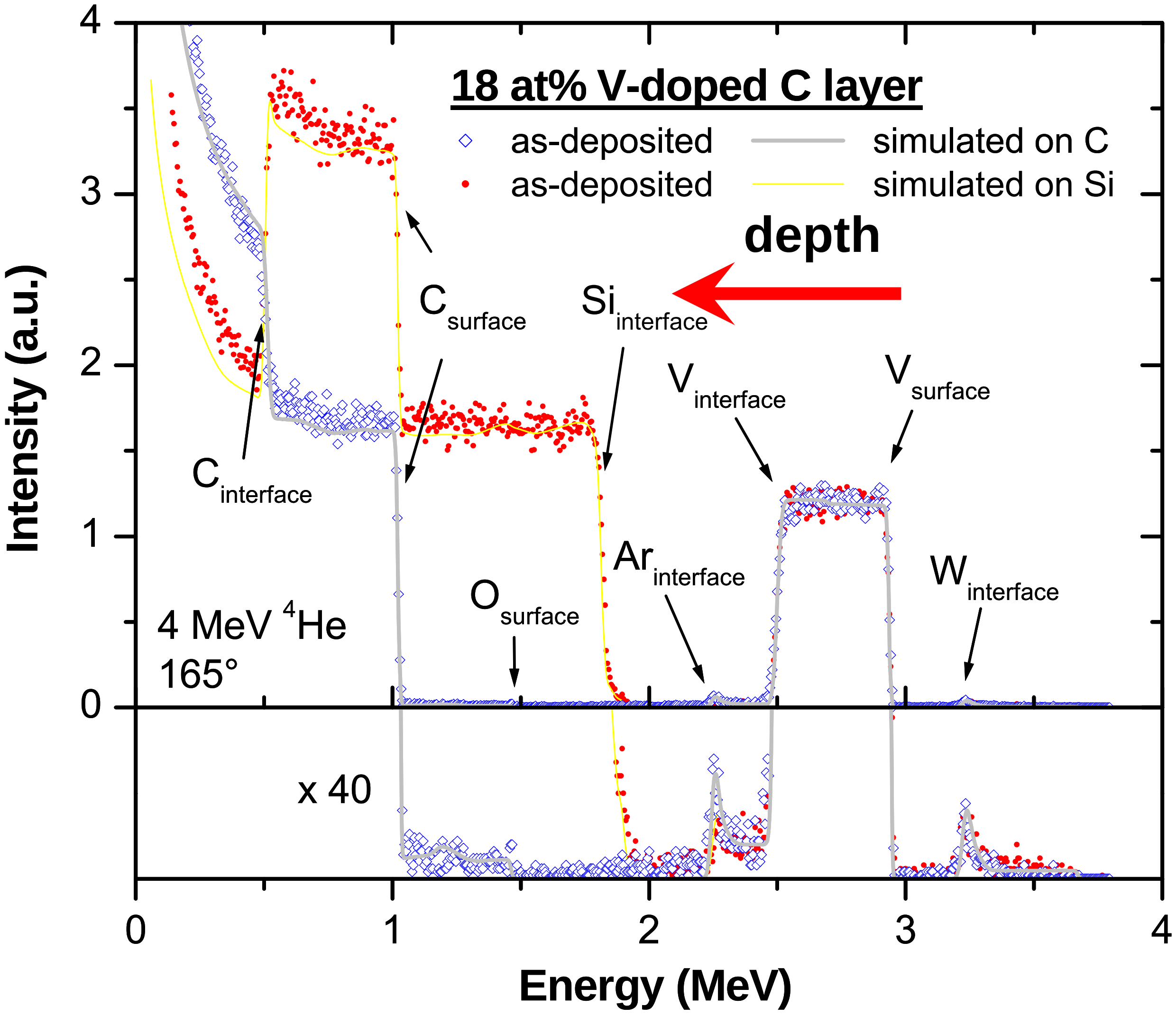
  - **dopant** (**W**, Ti, V, Zr)
  - **concentrations** (0 - 20 %)

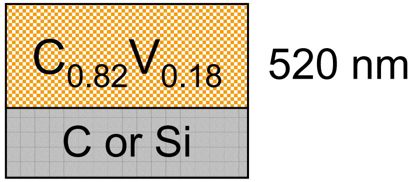
- **annealing:** 500-1300 K (0.25 & 2 h)
  (e.g. carbide formation, diffusion)



composition, homogeneity, morphology

Composition, distribution & impurities (RBS)





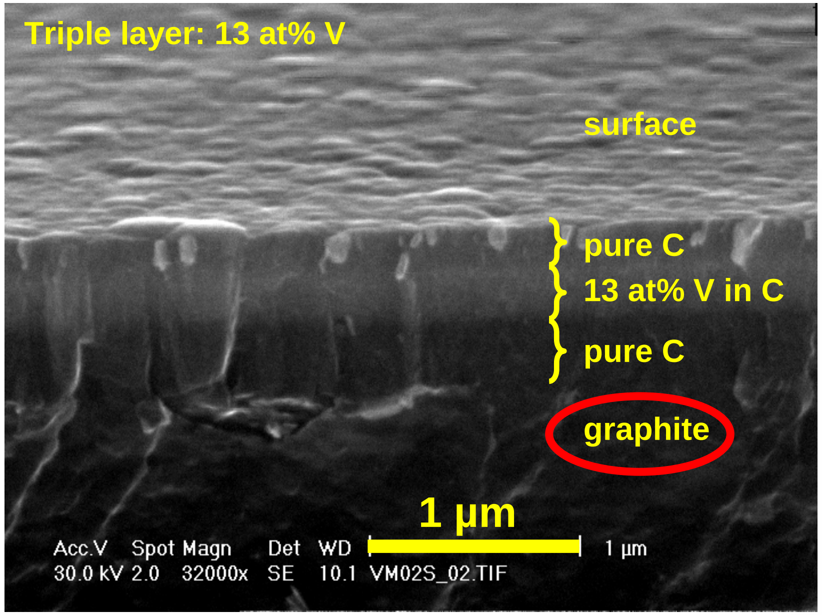
- dopant homogeneity
- O < 1 at%
- Ar ~ 1 at%

  released by annealing
- W < 0.01 at%

  unusual

H-RBS

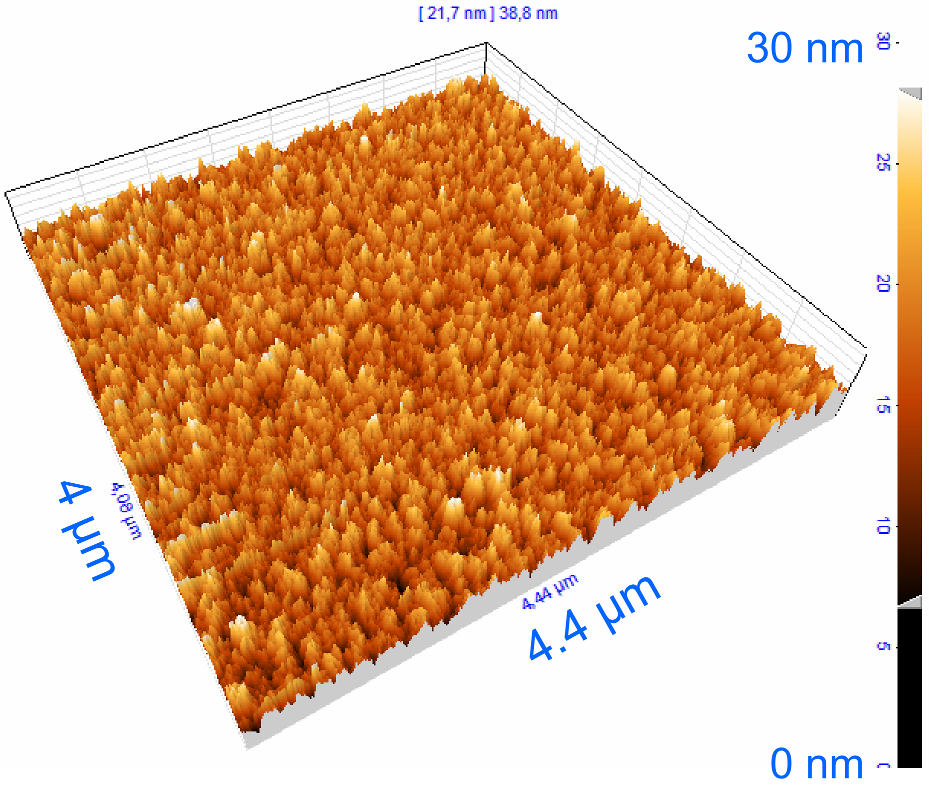
Layer morphology (SEM, AFM)



- homogeneous, columnar growth
- structures size triggered by substrate roughness
- no change in columnar growth by dopant

- **<u>no significant changes by annealing</u>**

Single layer: 7.5 at% Zr on Si



Outline

Chemical bonding of metals and crystallinity

Local atomic environment (XAS: EXAFS)

EXAFS: Extended X-ray absorption fine structure

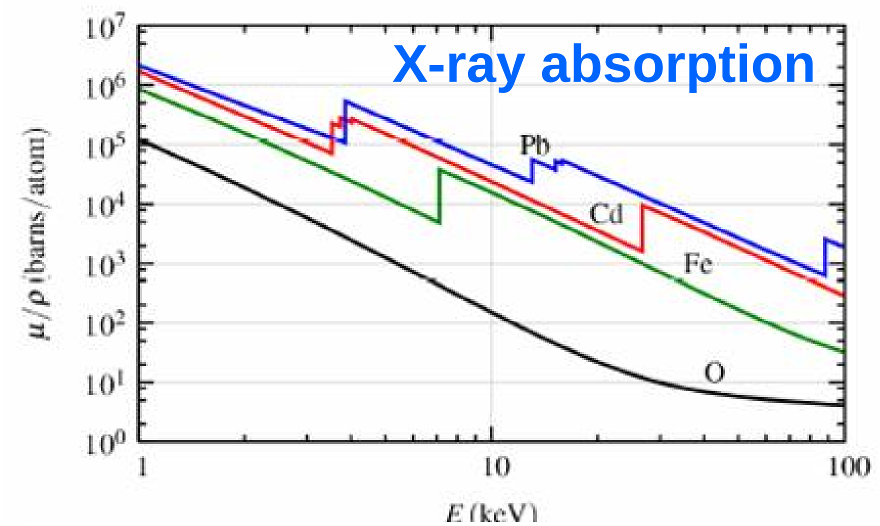
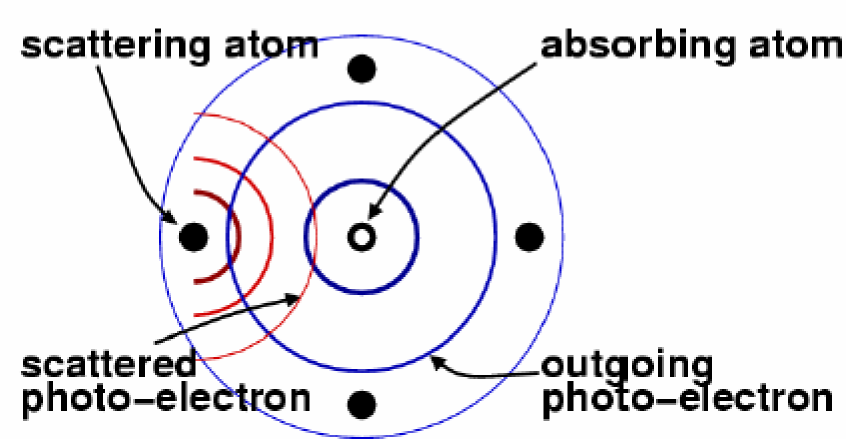
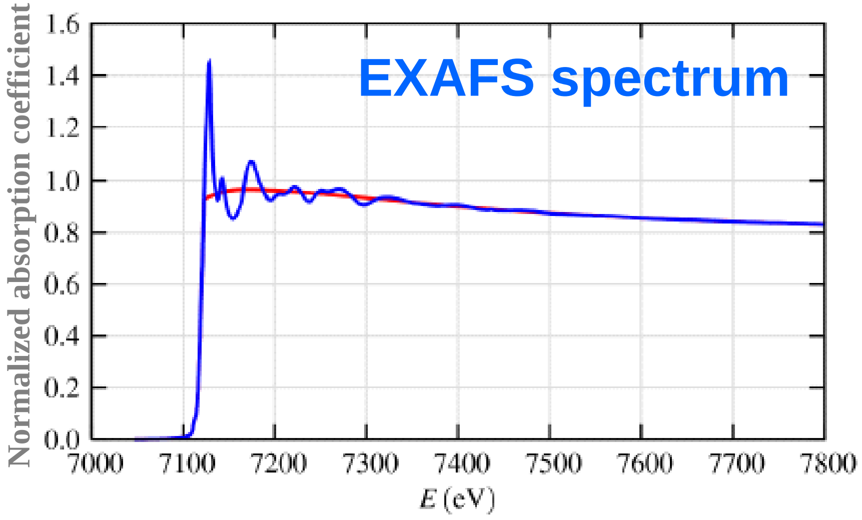


Photo electrons

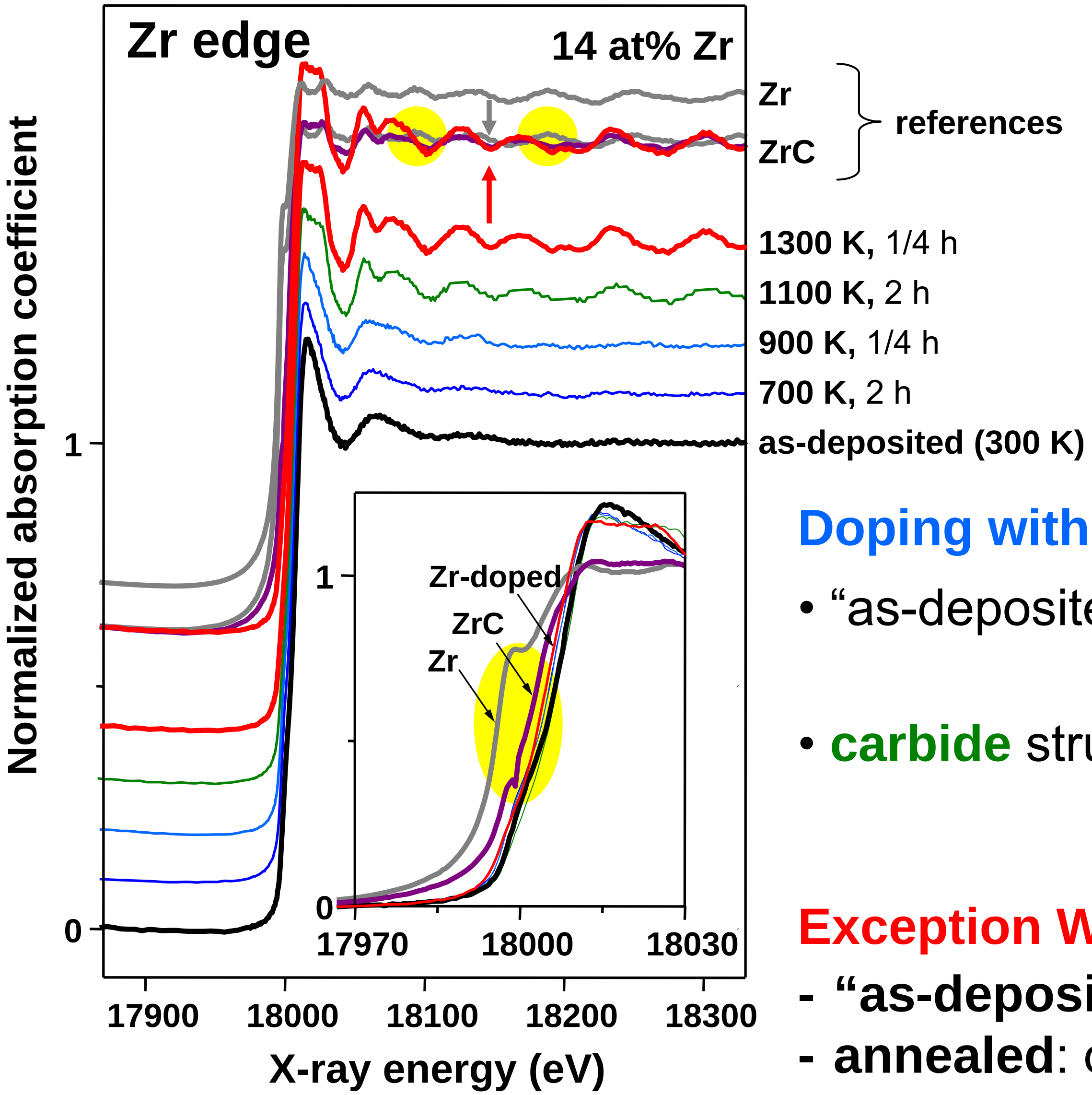


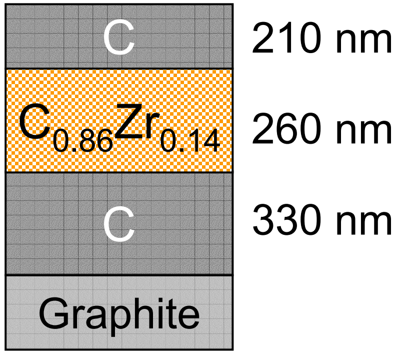


Interference / Oscillations ⇨ EXAFS

Information about the local atomic environment of the absorbing atom (Neighboring atoms N, distance R, disorder σ)

Local atomic environment (XAS: EXAFS)





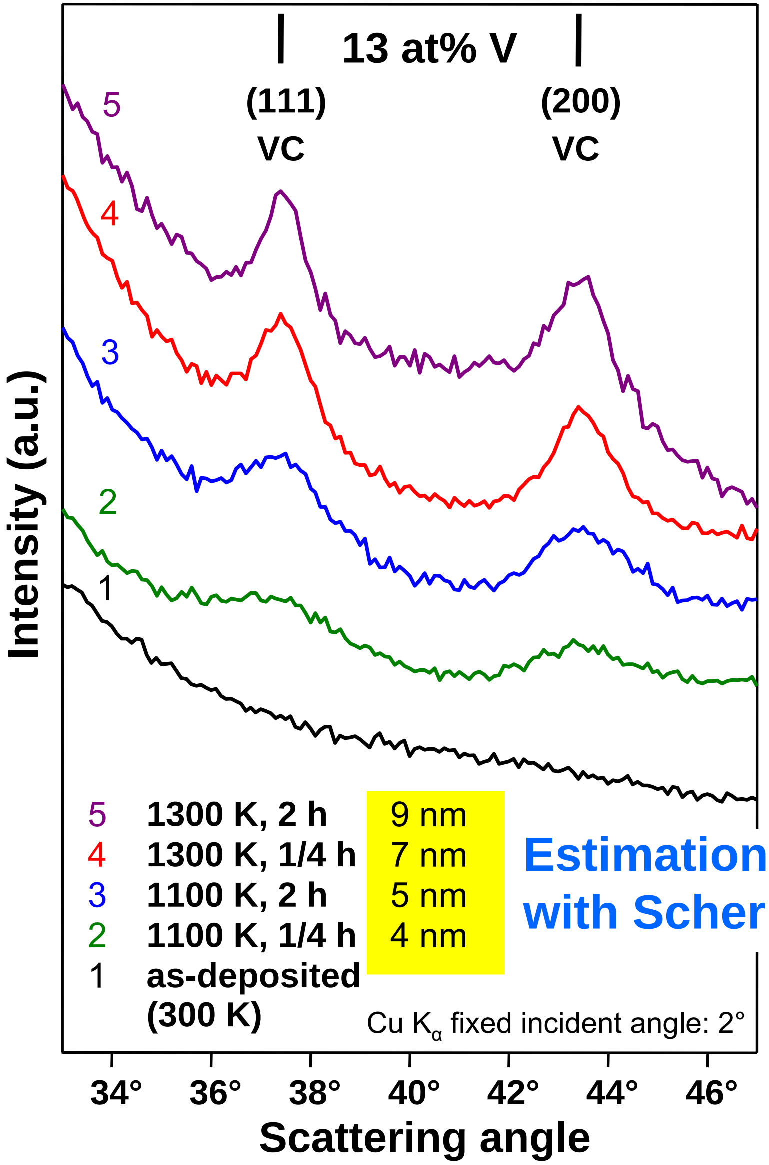
Doping with Ti, V & Zr

- “as-deposited”: - **amorphous** / disorder
  - **non-metallic** state
- **carbide** structure already at 1100 K (qualitative ⇨ quantitative)

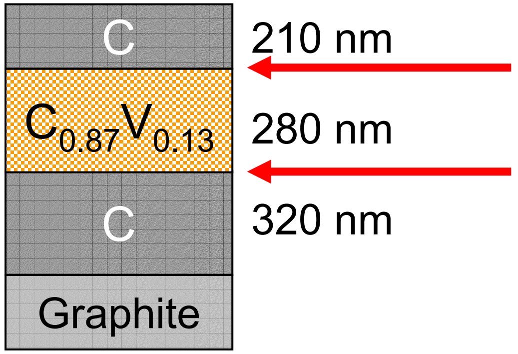
Exception W-doping:

- **“as-deposited”**: higher **order**
- **annealed**: only slight changes

Crystallinity of layers (XRD): annealing



Estimation of crystallite size with Scherrer's formula



Diffusion: <20 nm (RBS)

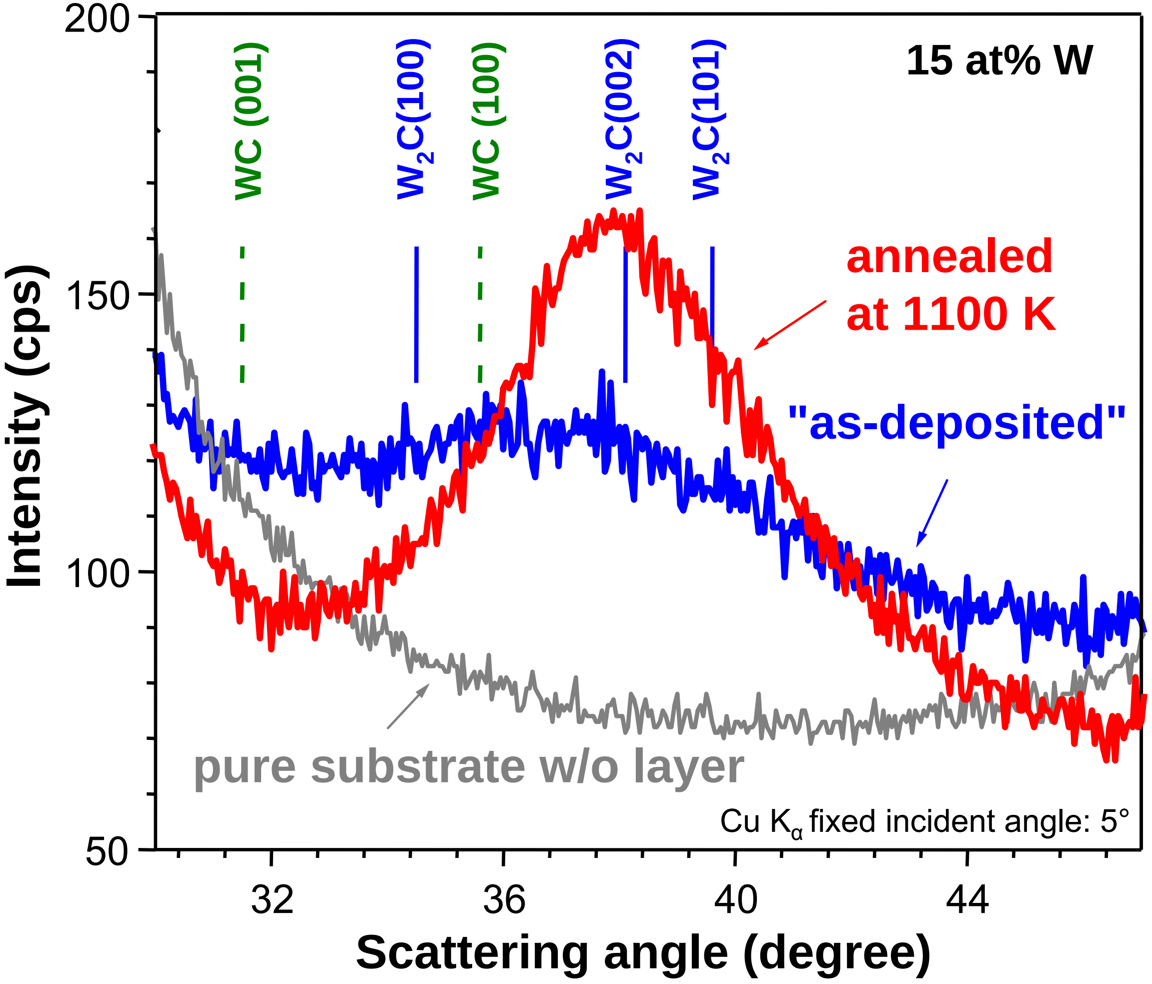
Doping with Ti, V & Zr

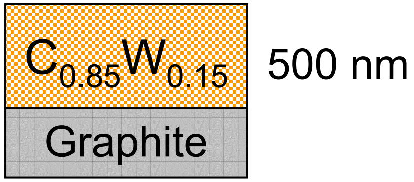
atomically deposition ➔ crystallite growth

- **carbide formation** after annealing (carbon-poor TiC, VC, ZrC)
- crystallite size increasing with T and t

↳ **exception W-doping**

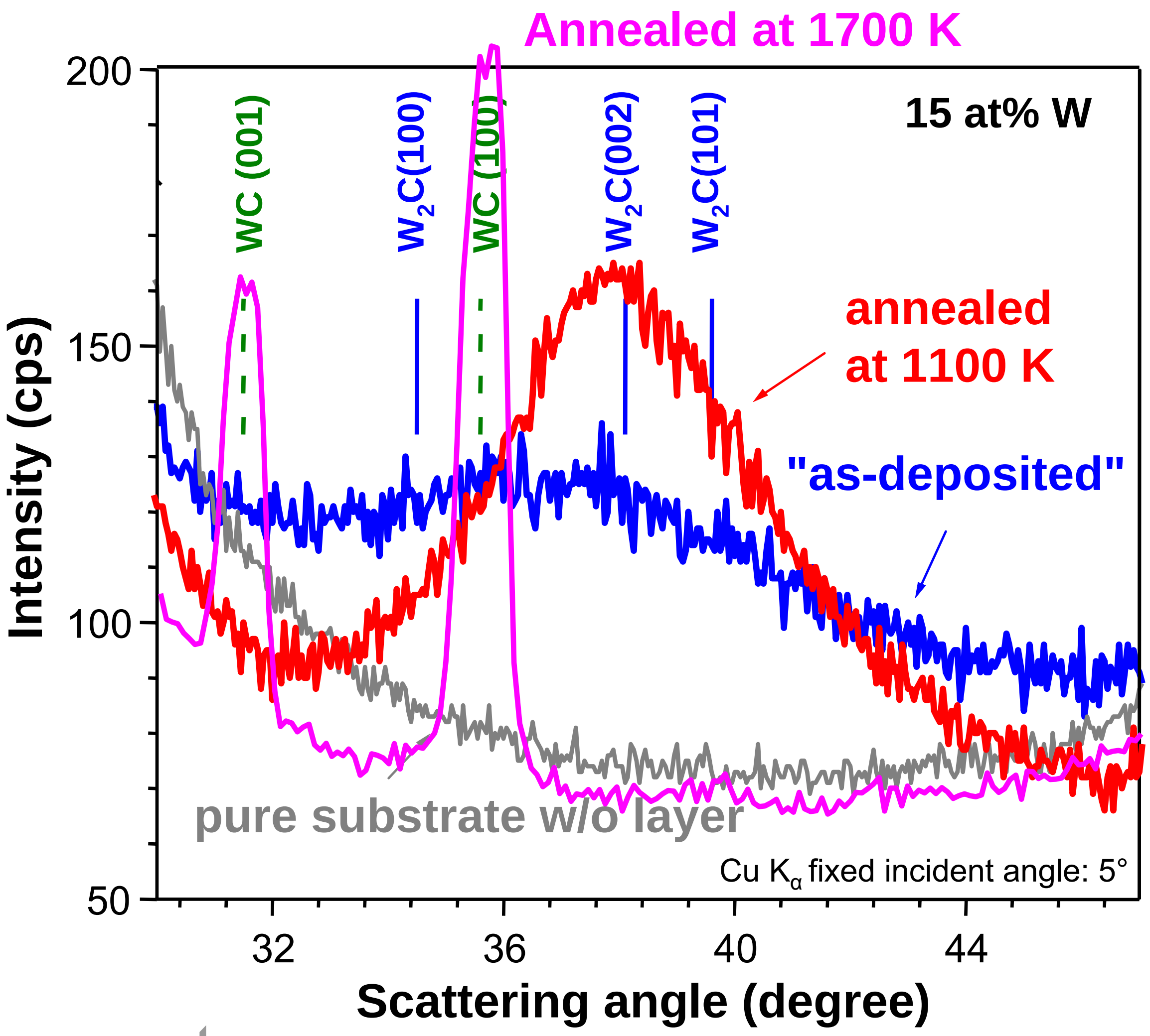
Crystallinity of W-doped layers (XRD)

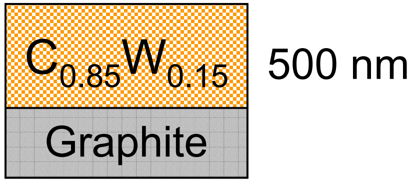




- already “as-deposited” show peak
- sub-carbide (**W_2C**) instead of carbide (**WC**) more pronounced after annealing
- grain size: **~ 2 nm** (always)
  (estimation with Scherrer’s formula)

Crystallinity of W-doped layers (XRD)





- already “as-deposited” show peak
- sub-carbide (**W_2C**) instead of carbide (**WC**) more pronounced after annealing
- grain size: **~ 2 nm** (always)
  (estimation with Scherrer’s formula)

Annealing at 1700 K

↳ **WC** ➔ larger grains
>20 nm

TEM

Outline

Chemical erosion

Erosion Experiments: High Current Ion Source

Experimental setup

- mono-energetic mass-separated ion beam:
  30 eV, 200 eV, 1 keV D (D_3^+)
- flux: ~10^{19} D/m^{2}s
- temperature controlled (RT-1450 K)

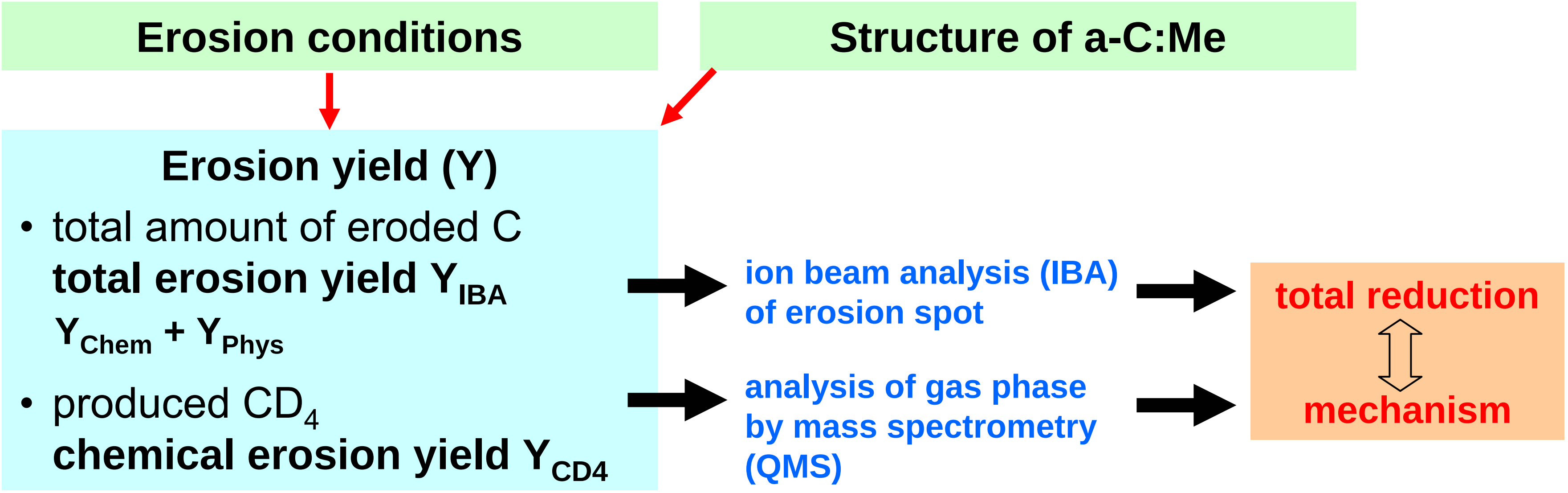
Experimental procedure

- annealing to 1100 K ⇨ **carbide grains: W 2 nm, other 4-8 nm**
- D bombardment of a-C:Me
  - D energy: **30 eV / 200 eV**
  - temperature: **fixed RT / ~750 K** 3 - 7 × 10^{23} D/m^2
    stepwise increased: RT - 1000 K
    4-7 × 10^{21} D/m^2 per step, total <10^{23} D/m^2

} **two types of measurements**

Concept of Erosion Yield

Metal-containing amorphous carbon films (a-C:Me)



Erosion conditions

Structure of a-C:Me

Erosion yield (Y)

- total amount of eroded C
  total erosion yield Y_{IBA}
  $Y_{Chem} + Y_{Phys}$
- produced CD_4
  chemical erosion yield Y_{CD4}

ion beam analysis (IBA) of erosion spot

analysis of gas phase by mass spectrometry (QMS)

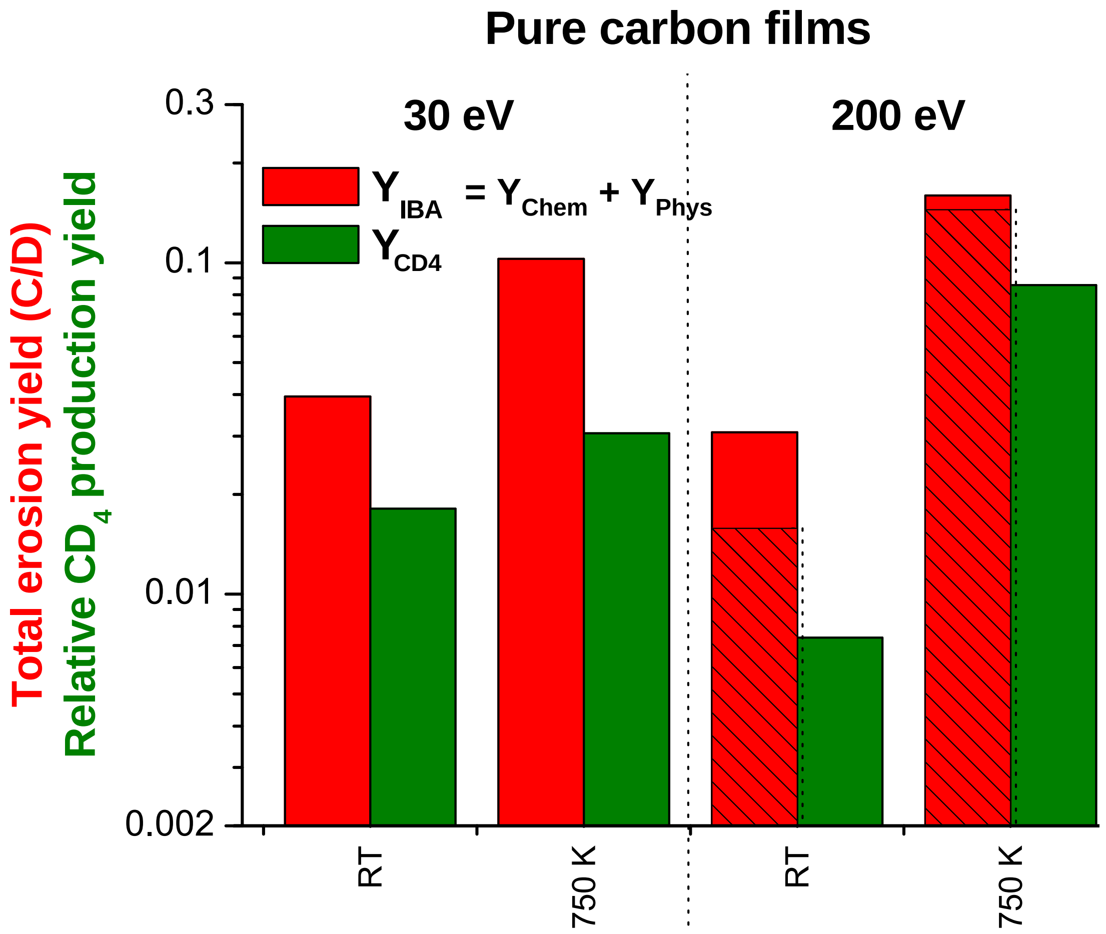
total reduction
⇕
mechanism

$$Y = \frac{\sum C_{removed}}{\sum D_{incident}}$$

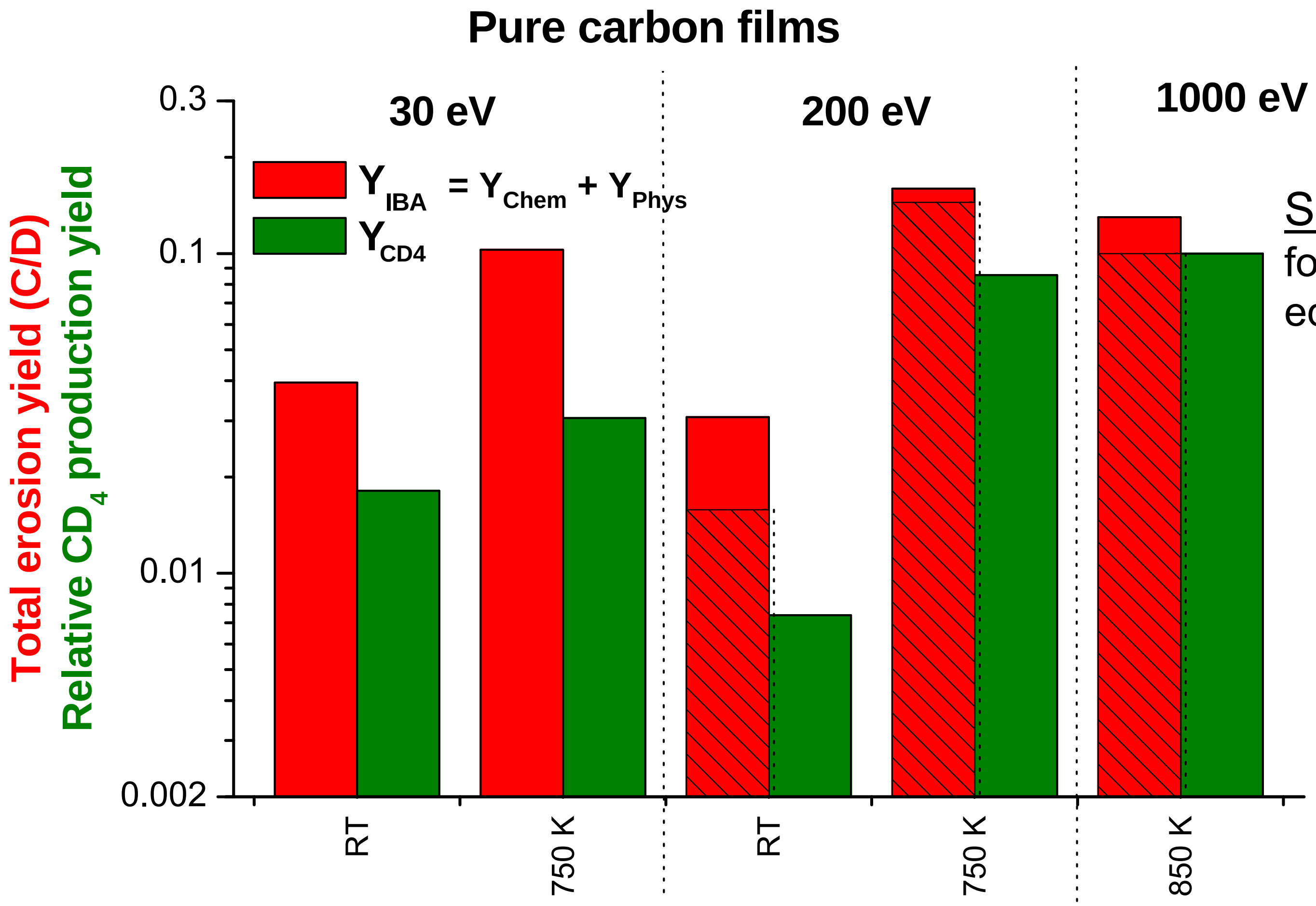
Influence of doping on produced hydrocarbons expected

⇒ reflected in amount of produced CD_4

Results: Erosion Yield IBA / QMS



Results: Erosion Yield IBA / QMS


Pure carbon films

<u>Scaling</u>: CD_4 production for 1 keV D at T_{max} equal Y_{Chem} (c = 1)

$$Y_{Chem} = c\, Y_{CD4}$$

$$c = 1.2 - 4$$

<u>D:</u>

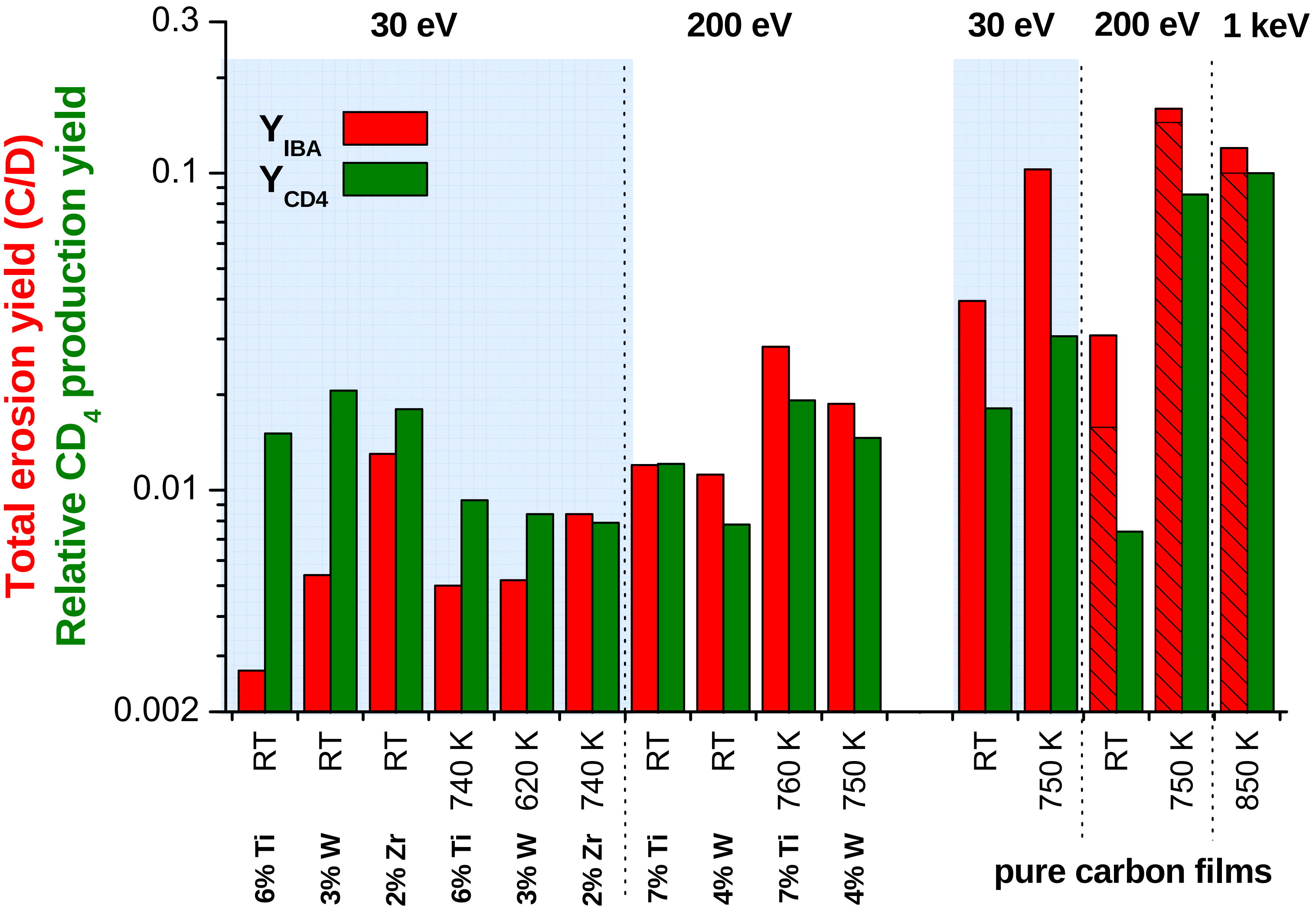
Roth '83:	3
Mech '98:	~2 (200 eV)

<u>H:</u>

Roth '83:	4
Yamada '87:	2
Davis '88:	1.2
Mech '97:	~2 (200 eV)

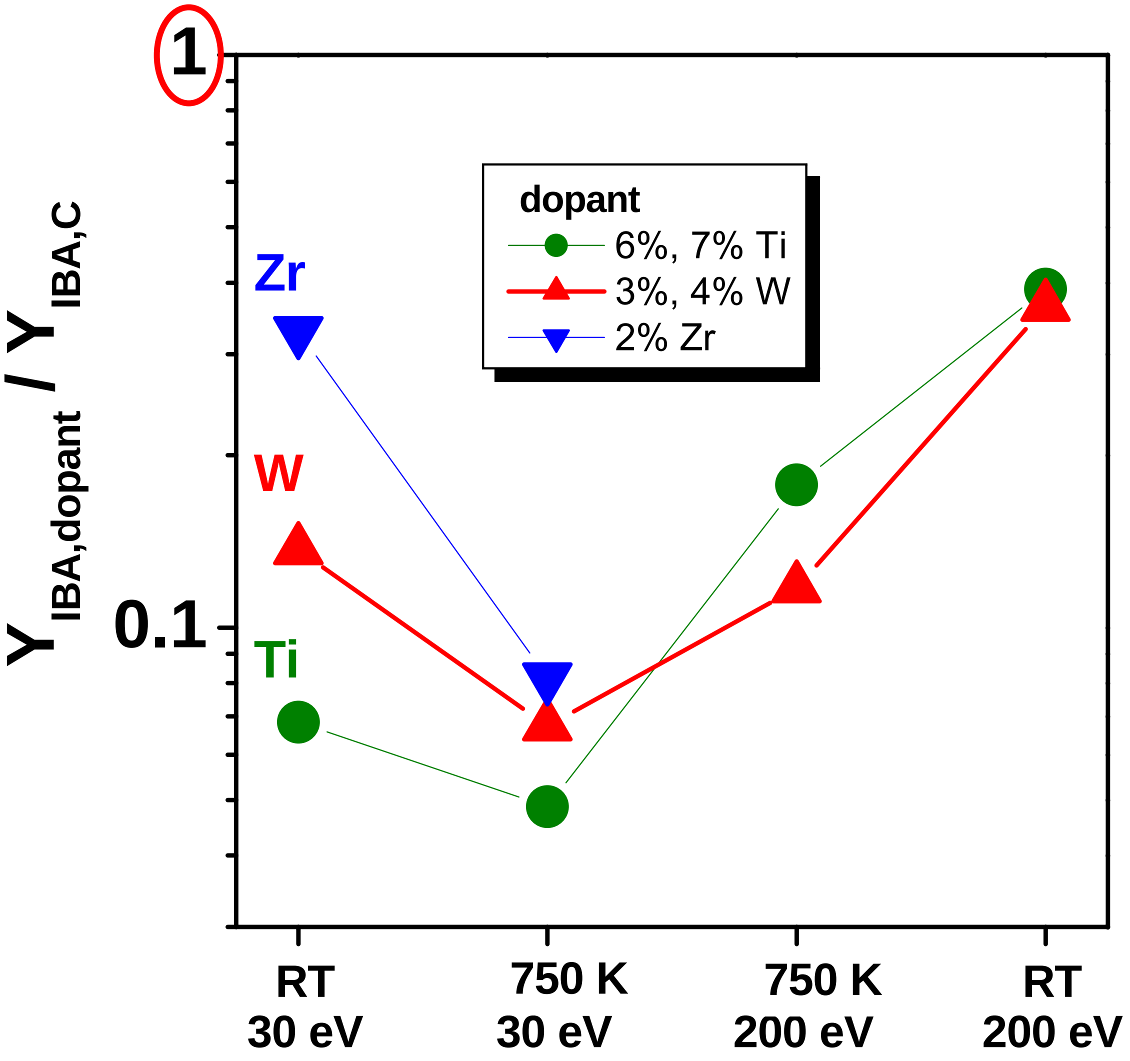
- $Y_{hot} > Y_{RT}$ (well known)
- Y_{CD4} always smaller than Y_{IBA} ⇨ less CD_4 produced compared to 1 keV at T_{max}

Comparison Erosion Yield IBA / QMS



Total erosion yield Y_{IBA}: Effect of doping

Carbon erosion yield

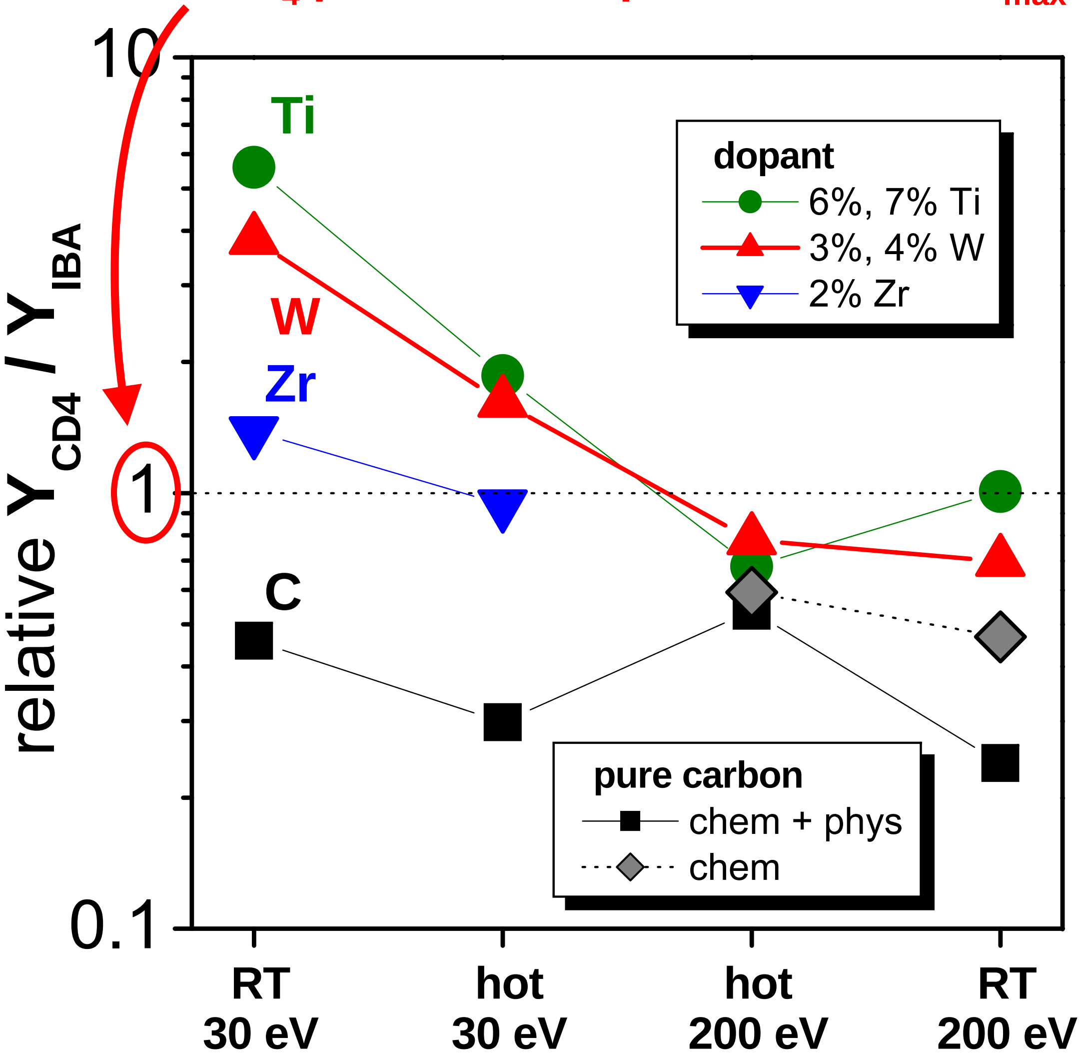


- reduced total erosion for all doped samples
- reduction most prominent at high temperatures and 30 eV (for Ti only 5 %)
- reduction changes with metal content / type
- metal erosion observed for 200 eV

  ⇘ comparable to yields for carbides

Comparison Erosion Yield QMS / IBA

CD_4 production equal to 1 keV D, T_{max} (Y_{Chem} = 1.2 - 4 Y_{CD4})



- Y_{CD4}/Y_{IBA} < 1 for pure C

  ⇘ more C_xD_y / radicals
- ratio always higher for a-C:Me compared to C
- 200 eV: $Y_{CD4}/Y_{IBA} \leq 1$

  ⇘ more C_xD_y / radicals
- 30 eV: $Y_{CD4}/Y_{IBA} \geq 1$

  ⇘ more CD_4 production

compare to
published factors (1.2 - 4)

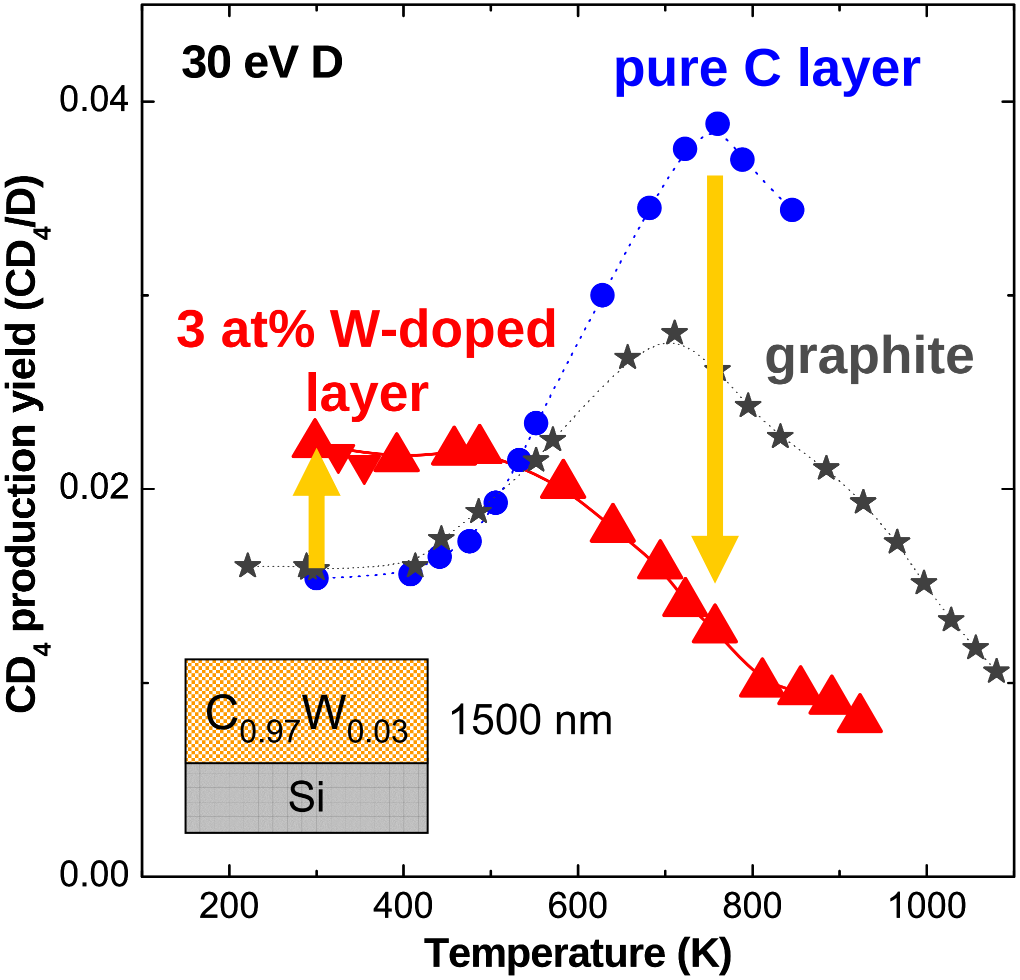
⇘ mainly CD_4

Temperature dependence of chemical erosion (QMS)

Doping with W (V, Ti, Zr)

- mass- & energy-separated ion beam (30 & 200 eV/D)
- detection of volatile erosion species (CD_4)
- **CD_4 production** yield
  - strong reduction at elevated temperatures
  - enhancement at RT

  ↳ **total yield reduced**

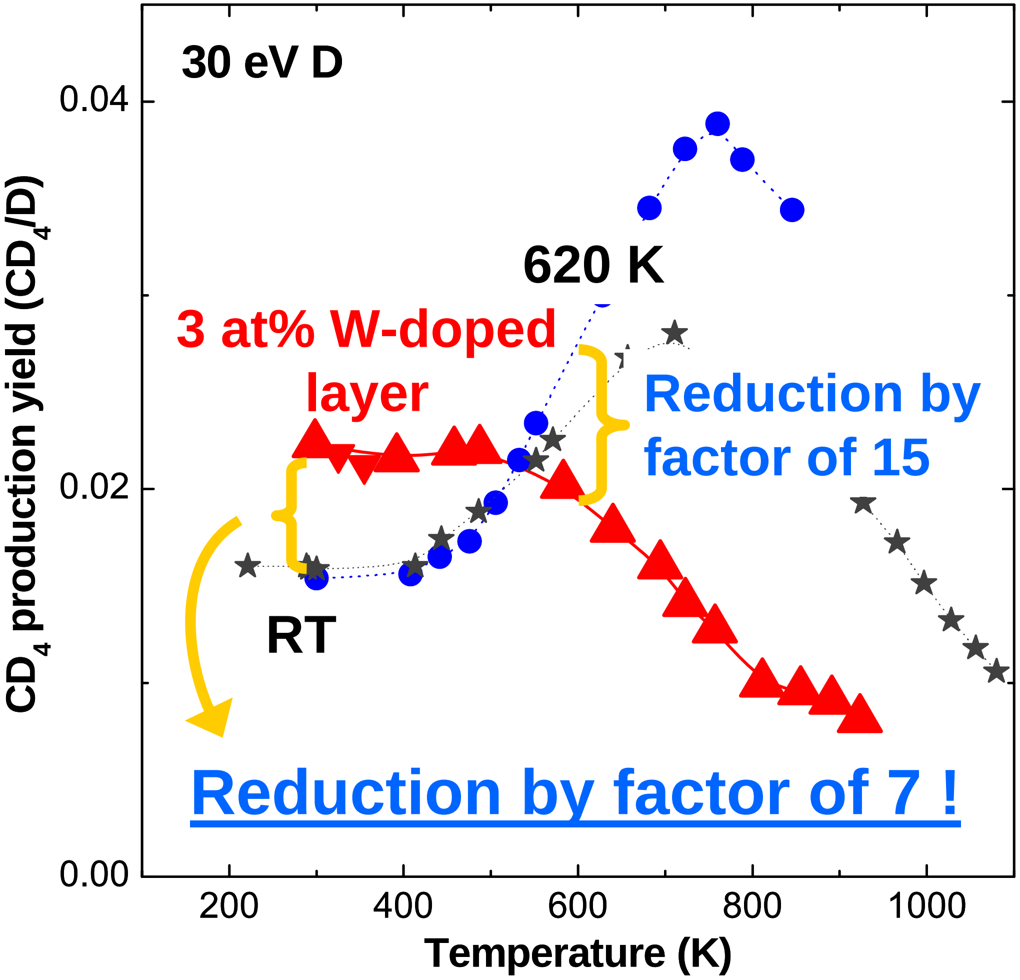


Temperature dependence of chemical erosion (QMS)

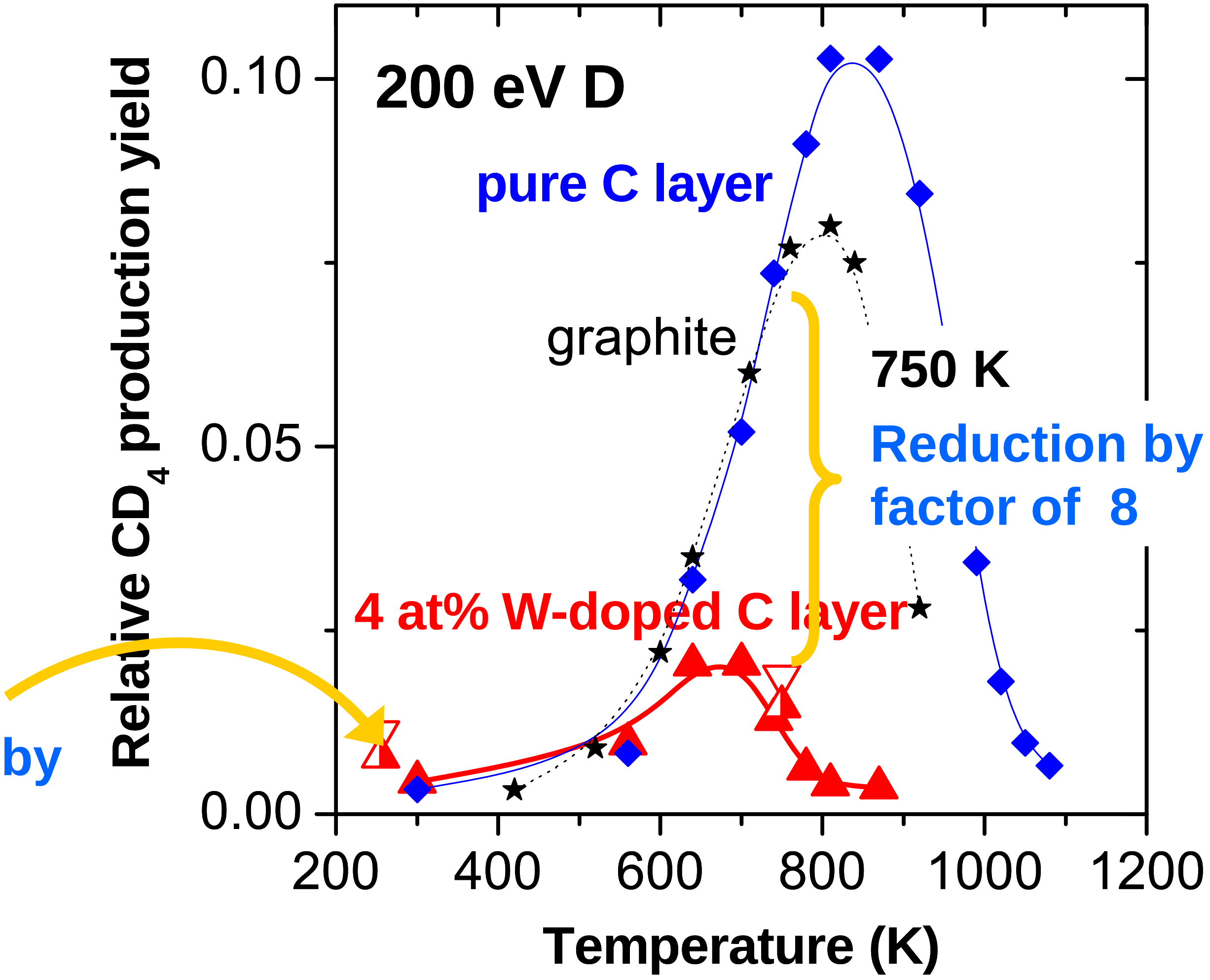
Doping with W (V, Ti, Zr)

- mass- & energy-separated ion beam (30 & 200 eV/D)
- detection of volatile erosion species (CD_4)
- **CD_4 production** yield
  - strong reduction at elevated temperatures
  - enhancement at RT
    - ⇘ **total yield reduced**
    - ⇘ **distribution of erosion products changed**

jump



Temperature dependence of 200 eV D



750 K

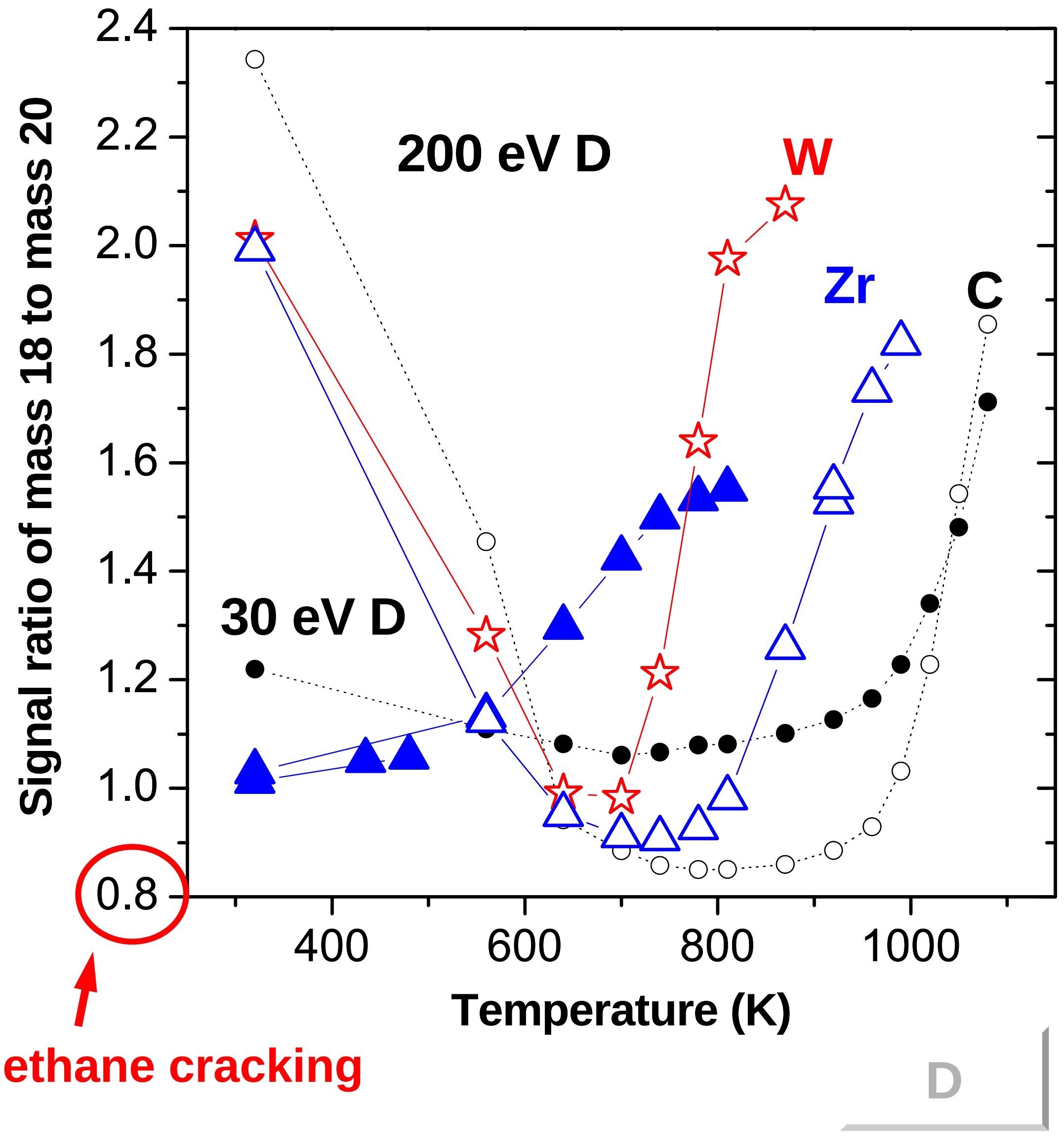
Reduction by factor of 8

RT

Reduction by factor of 3

jump

Ratio of QMS signal: Temperature dependence



Methane cracking

Ratio mass 18 / mass 20:
- indicator of CD_3 or cracking of heavier C_xD_y
- changes of ratio
  ↳ change in distribution of erosion species

200 eV:
- only methane at T_{max}
- C: comparable to 1 keV
- doping:
  ↳ changes at high T

30 eV:
- mainly methane at RT
- doping:
  ↳ changes at high T
  ↳ more CD_4 at RT

Conclusion

- **production** and **characterization** of nano-structured metal-containing amorphous carbon films (0 – 20 at% Me) as model for mixed re-deposited layers

- **chemical erosion** strongly affected by doping
  - **total erosion yield drastically reduced**

    (factor of ~10 at elevated temperatures; at RT at least factor of 3)

  - doping changes **distribution of erosion species** to more CD_4 production (30 eV)

⇨ **using only the signature of one species leads to wrong erosion yields**
(e.g. spectroscopic investigations on strongly polluted surface),
but CD_4 is may be still indicator for variations

Discussion / Questions

Contributors:

Ch. Adelhelm,

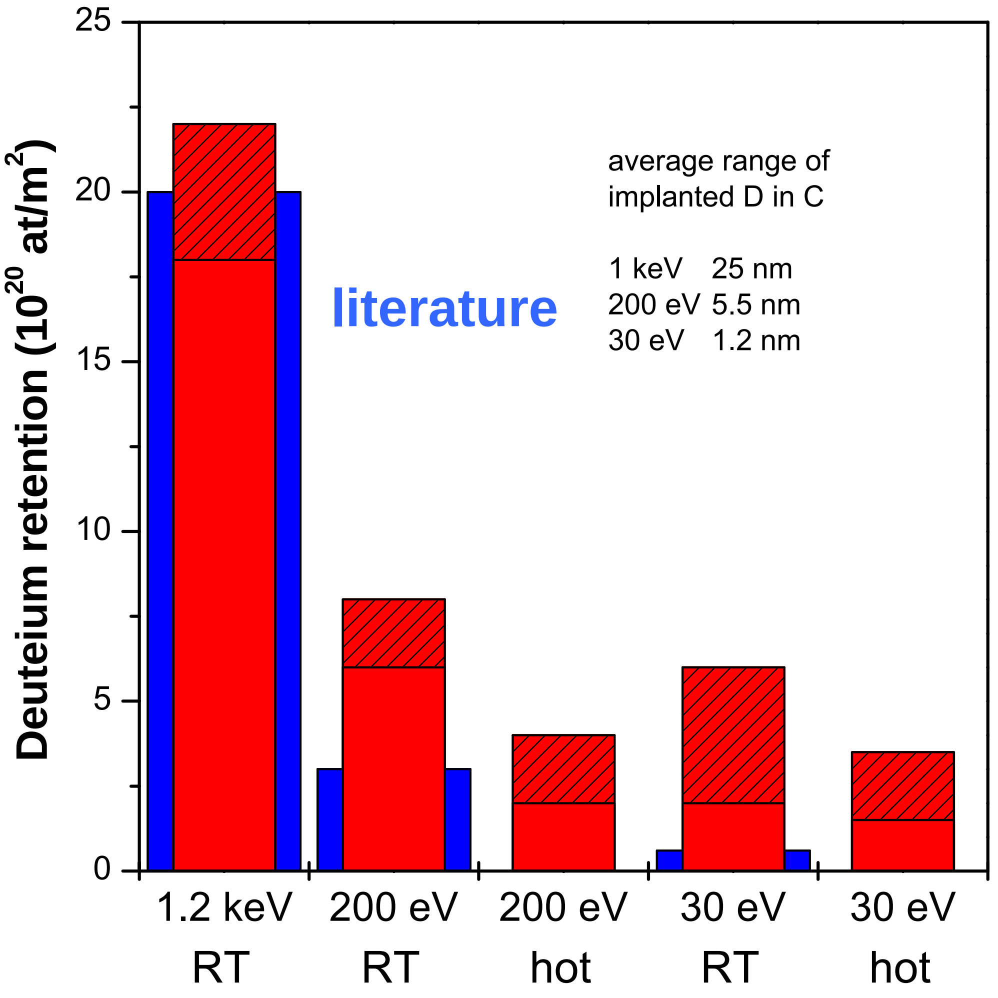
E. de Juan Pardo, J. Roth,

S. Lindig, A. Herrmann, B. Cieciwa, I. Quintana Alonso, B. Dubiel, E. Welter …

The end

Deuterium retention

Deuterium content determined by NRA



- fixed erosion condition
- fluence 3 - 7 × 10^{23} D/m^2