W dust formation in plasmas in contact with tungsten surfaces: lessons learned from laboratory experiments...

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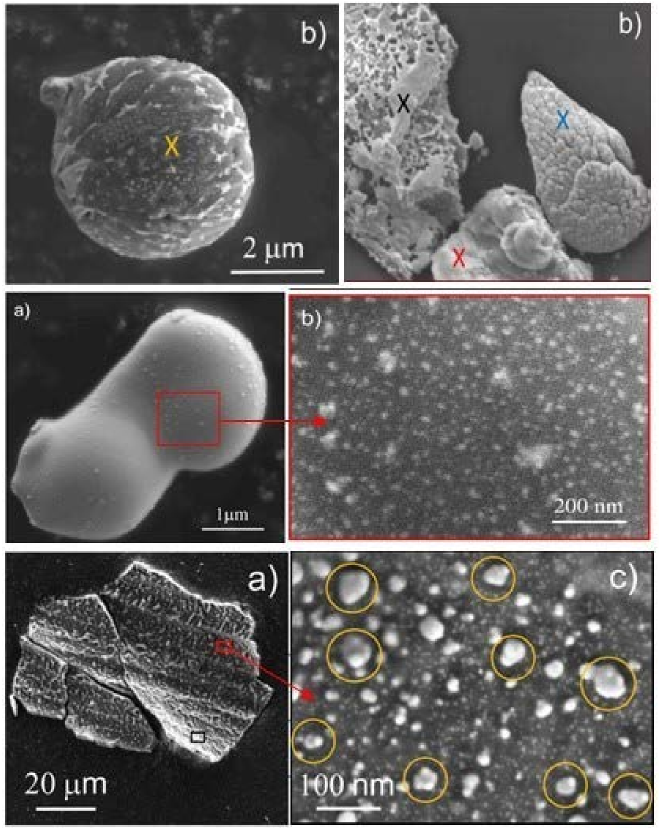
PWIE workshop on Plasma-Wall interaction in full W devices,
September 17-19 2024, Aix en Provence, dinescug@infim.ro

Dust in Tokamak discharges - nanoparticles collected in WEST



Example of dust particles collected on the WEST divertor;

Two distinct dust populations:

- W particles with micrometers up to tens of micrometers size
  caused by the off-normal events (droplets emitted due to high thermal load) or delamination of W coatings;

- W particles with dimensions in the range of nanometers
  caused by condensation of vapors above microsize particles or to ion metallic clusters growing in presence of W sputtering.

S. Peillon et al., Nuclear Materials and Energy 24 (2020) 100781

C. Arnas et al., Nuclear Materials and Energy 36 (2023) 101471

Laboratory dust study : managing discharges to explore separately the effects of melting and evaporation, of evaporation, of sputtering

- Tokamak discharges – simultaneous melting AND evaporation/vaporization AND sputtering;

- Microarcs – local deposition of energy at surface

Lessons learned

Excluding sputtering: Experiments where melting and vaporization counts

-leads to microparticles and nanoparticles
-microparticles are spherical, like solidified droplets

- Hollow Cathode Discharges –hot electrodes in plasma

Excluding melting: experiments under action of sputtering and evaporation

-leads to nanoparticles and microparticles
-microparticles formed from agglomerated nanoparticles

V. Marascu et al., Appl. Sci. **2020,** 10, 6870
V. Marascu et al., Mater. Res. Express **2020 7,** 065509
C. Stancu et al., Materials **2023,** 16, 6853
V. Marascu et al., Coatings **2023**, 13, 503

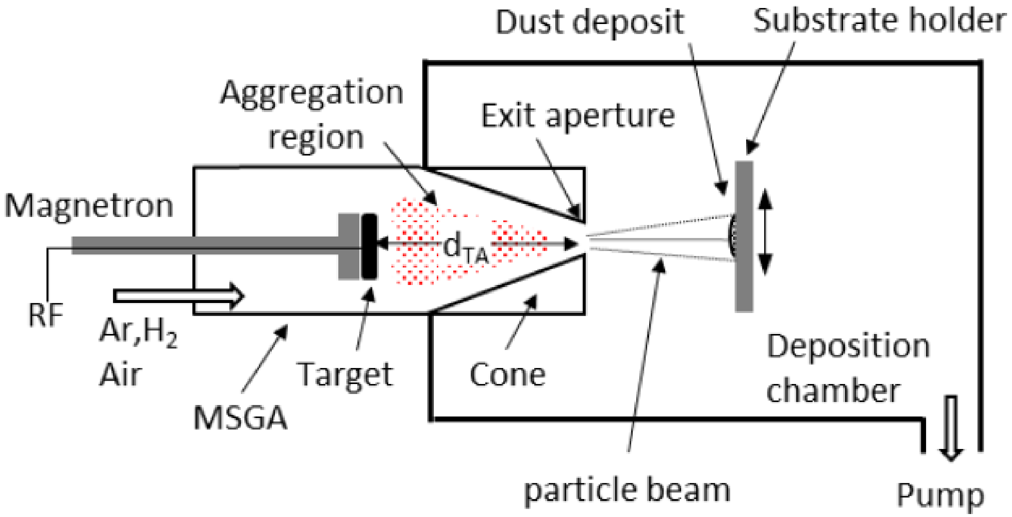
- Sputtering discharges

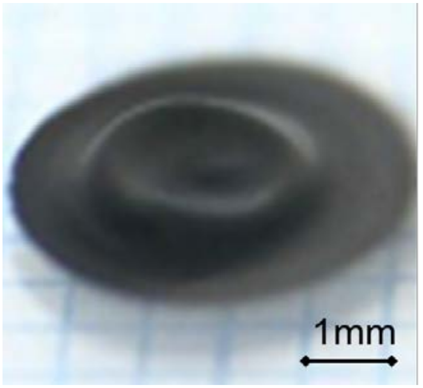
Excluding melting and evaporation: Experiments with only sputtering present

Focus on sputtering, magnetron discharges: no melting, no evaporation

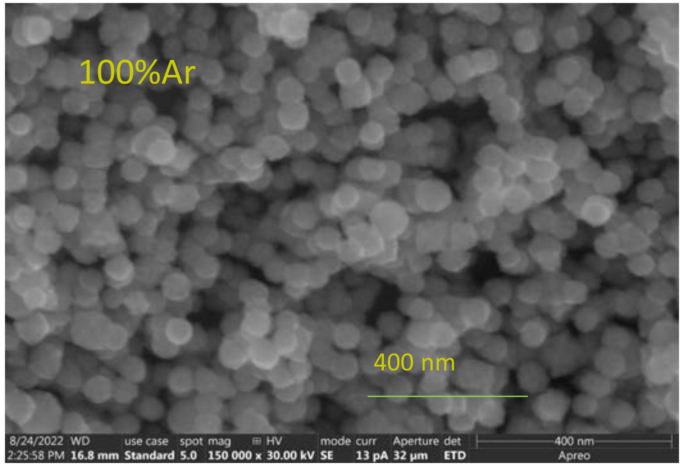
Making W nanoparticles by Magnetron Sputtering Gas Aggregation Technique – MSGA

W target; H_2, D_2 admixed with sputtering gases (Ar, Ne, Kr) and impurities (O_2, N_2, H_2O vapors); gas rates 0-10 sccm; p_{aggreg} ~ 0.7 mbar; p_{dep}~ 0.08 mbar; RF power: 80-130 W





spot on collector



SEM, particles

⇩ opportunity

Particles collected on substrate, can be extracted and studied separately

Focus on the effect of gases on dust formation rates and dust characteristics

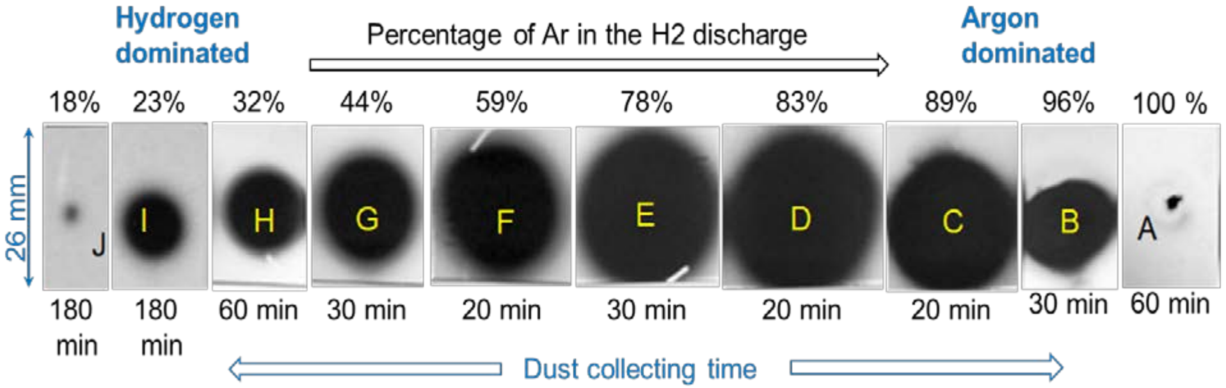
Example: characteristics and dust formation in H_2 plasmas injected with high-Z inert gases (Ar, Kr, ...) in relation with divertor plasma detachment (ENR project)

The impact of injecting Ar on the dust formation rates in hydrogen plasma

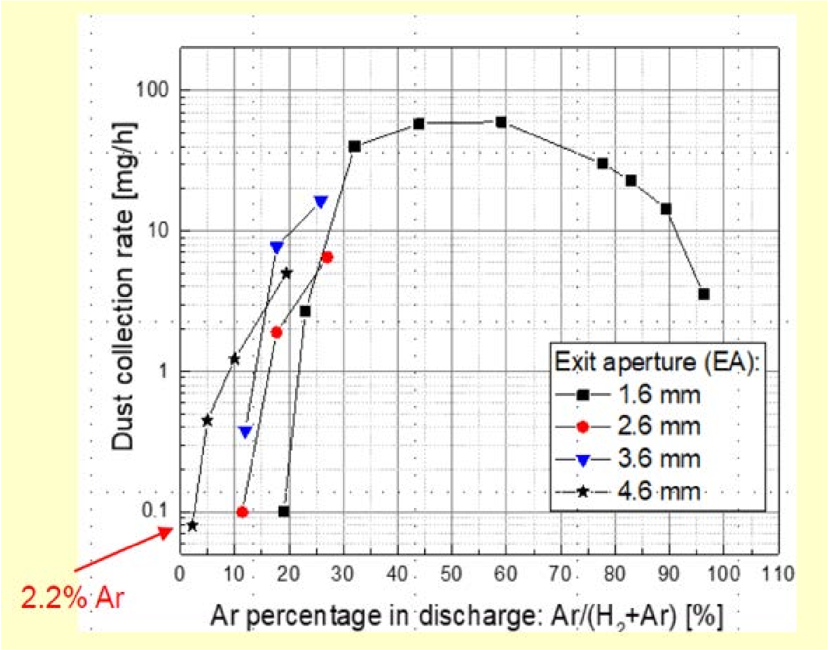
Variable, the percentage of Ar in H_2 + Ar plasma

- $Ar/(H_2+Ar)$: 0 –100 %
- p_{aggreg} ~8 $x10^{-2}$ mbar;
- p_{coll} ~ $5x10^{-3}$ mbar
- P_{RF} ~ 80 W
- Collecting time: 20 -180 min

Spots of collected particles(extraction aperture 1.6 mm)



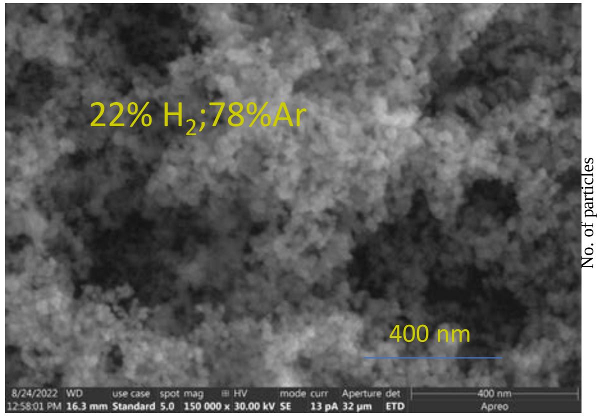
The mass of dust was measured by weighing the collectors before and after dust deposition

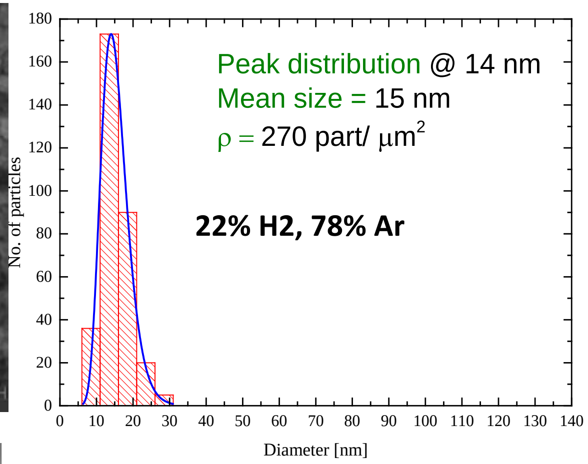


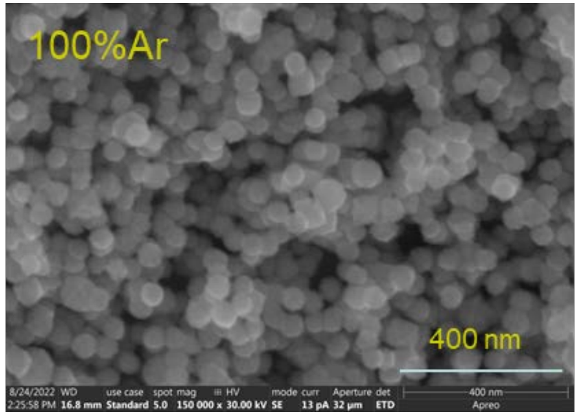
Collected dust rate upon the argon content

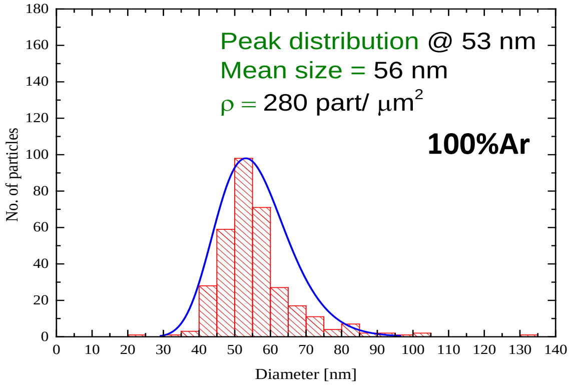
Conclusion: up to 20% injection of Ar in H_2 increases the dust formation rates more than 10^2 times.

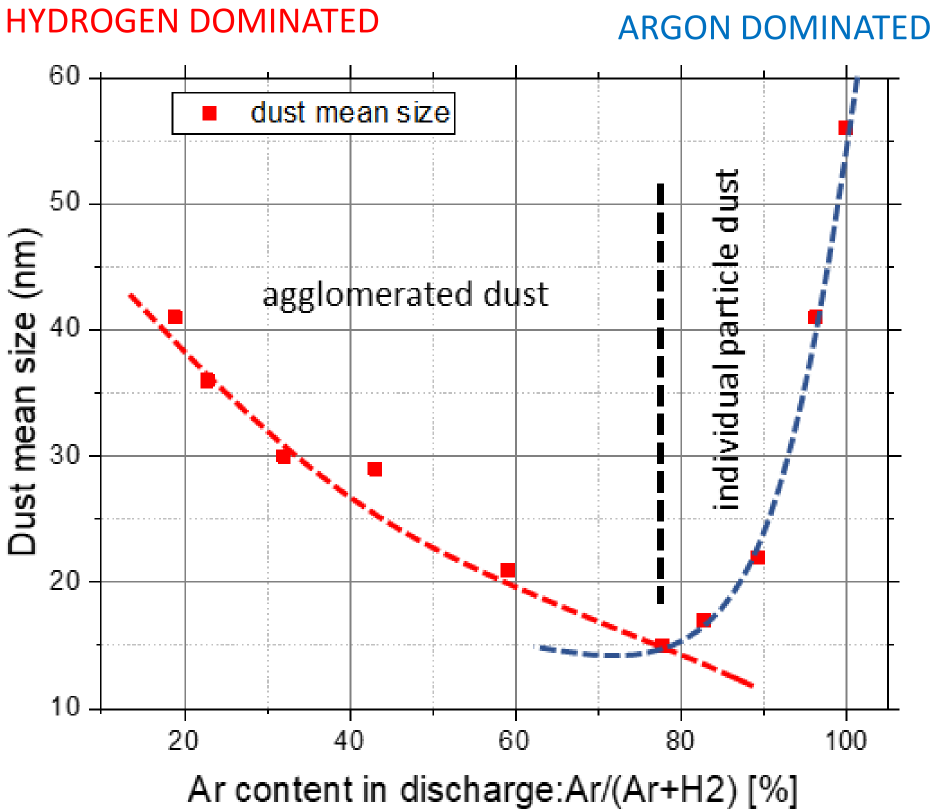
Evaluation of the effect of injecting Ar on particle size











Size of the collected dust upon the percentage of Ar injected in discharge (exit aperture of 1.6 mm).

Conclusions:

- Size of particles is much smaller in H_2 dominated discharges
- Fusing of particles is observed, agglomeration process is favored in H_2 dominated discharges;

Lessons learned from sputtering discharges

- Sputtering leads to W nanoparticles;
- Injecting Ar in hydrogen may increases drastically (x 100) the particles production rates;
- Nanoparticle size and dust morphology depends strongly upon the percentage of Ar injected in H_2:
  - hydrogen dominated discharges – small size and agglomerated dust
  - argon dominated discharges – higher nanoparticle size, individual particles in the dust

T. Acsente, et al. 2015, *Eur. Phys. J. D*, 69, 161;
T. Acsente, et al., 2017, *Materials Letters*, 200, p 121.
T. Acsente et al.. In: Mieno, T. , Hayashi, Y. , Xue, K. , editors, 2020, *Progress in Fine Particle Plasmas* https://www.intechopen.com/chapters/71477 doi: 10.5772/intechopen.9173
T. Acsente et al. 2021 *J. Phys. D: Appl. Phys*. 54 02LT01
T. Acsente et al. *Coatings* **2024**, 14, 964 (https://doi.org/10.3390/coatings14080964)

Summary of the results

Nanometric dust is common to all experiments where W vapors or atoms are present!

Questions:

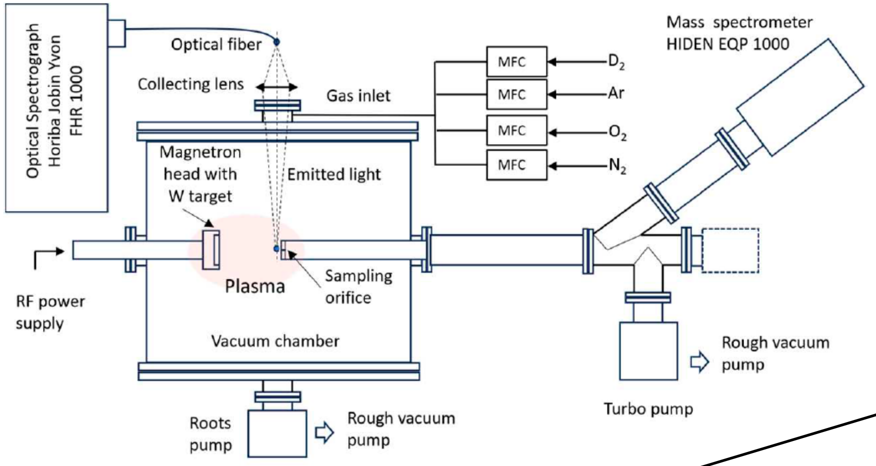
How nanometric dust is formed?

Can nanometric dust lead to micrometer size dust?

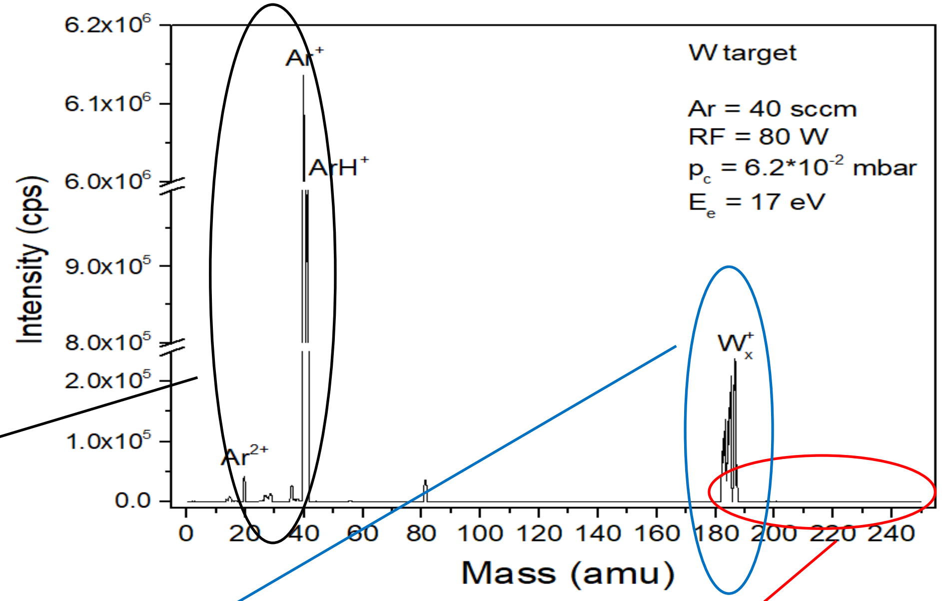
W species in sputtering W/H_2(D2) /Ar plasmas and their behavior upon injecting Ar in H_2 discharge

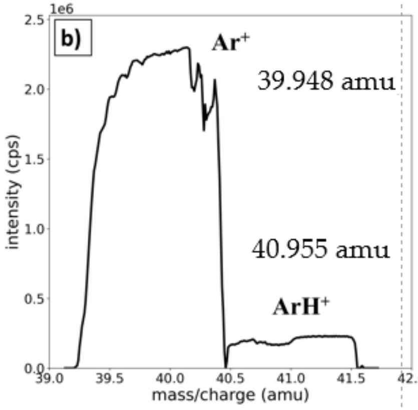
W species in sputtering H_2 (D_2)/Ar plasma – mass spectrometry

MS setup

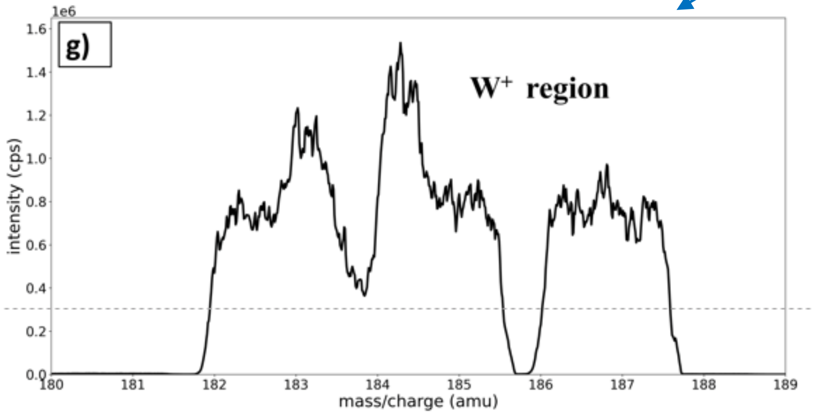


Mass spectrum of Ar plasma with W target

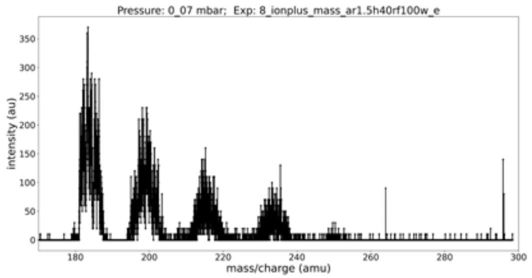




Focus on sputtering ion region (Ar^+ region)



Focus on sputtered species: W^+ region

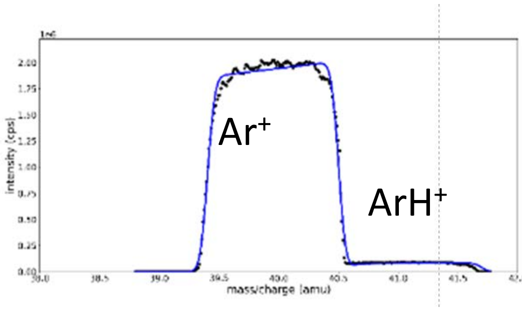


Noisy region 190-250 amu

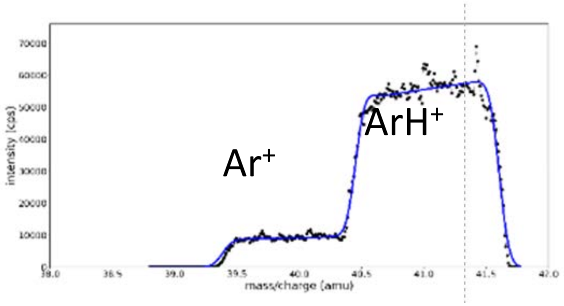
Will be discussed later!

Ar^+, ArH^+ zone: Behavior of sputtering ions upon Ar percentage in H_2

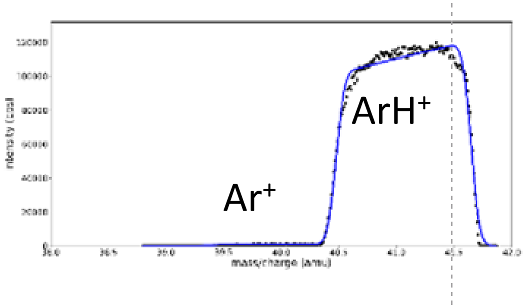
H_2 = 0%
(Ar only)



H_2 = 5%
Ar =95%

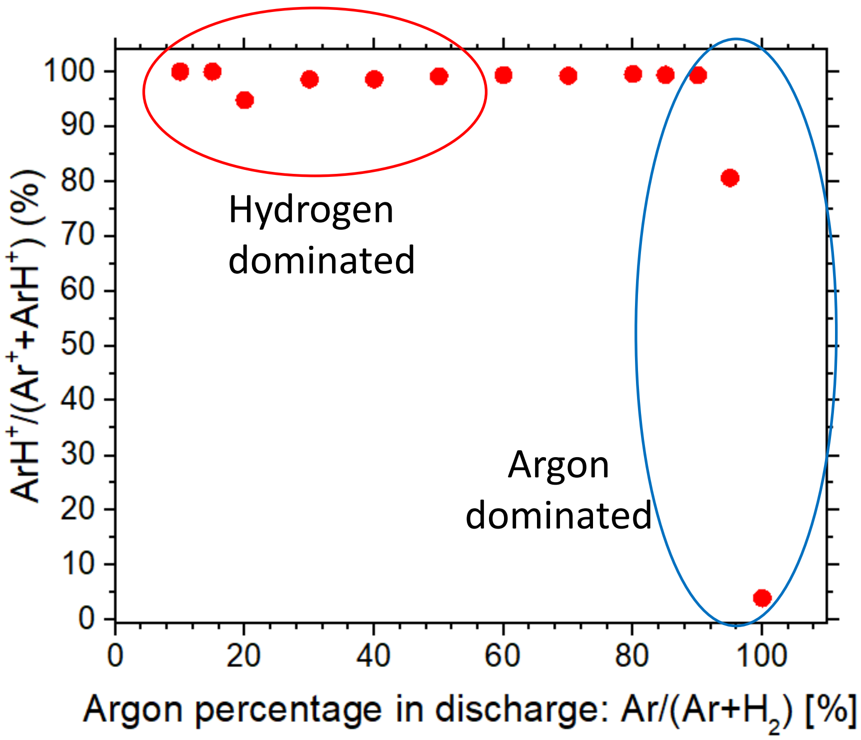


H_2 = 90%
Ar = 10%



H_2 causes the conversion of Ar^+ in ArH^+

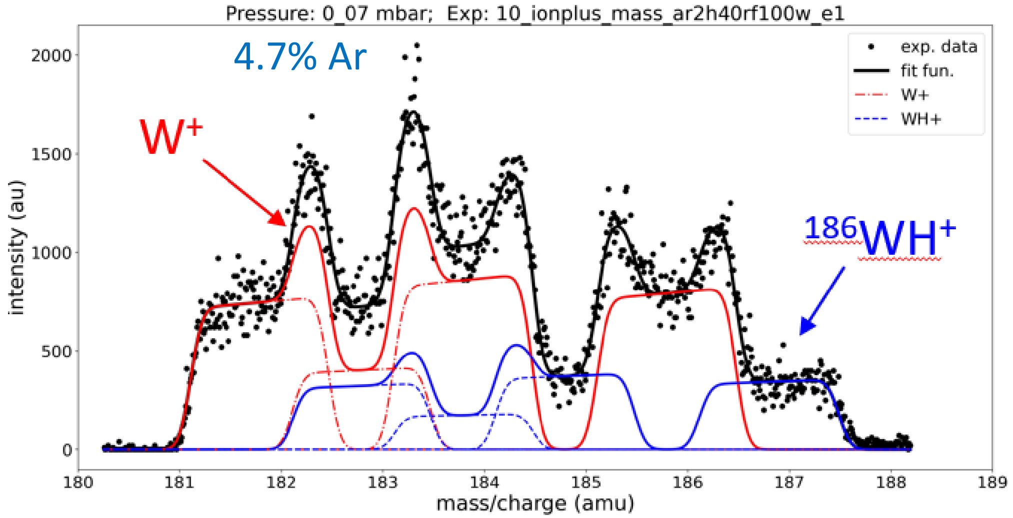
Evaluation of the ratio $\frac{ArH^+}{Ar^+ + ArH^+}$

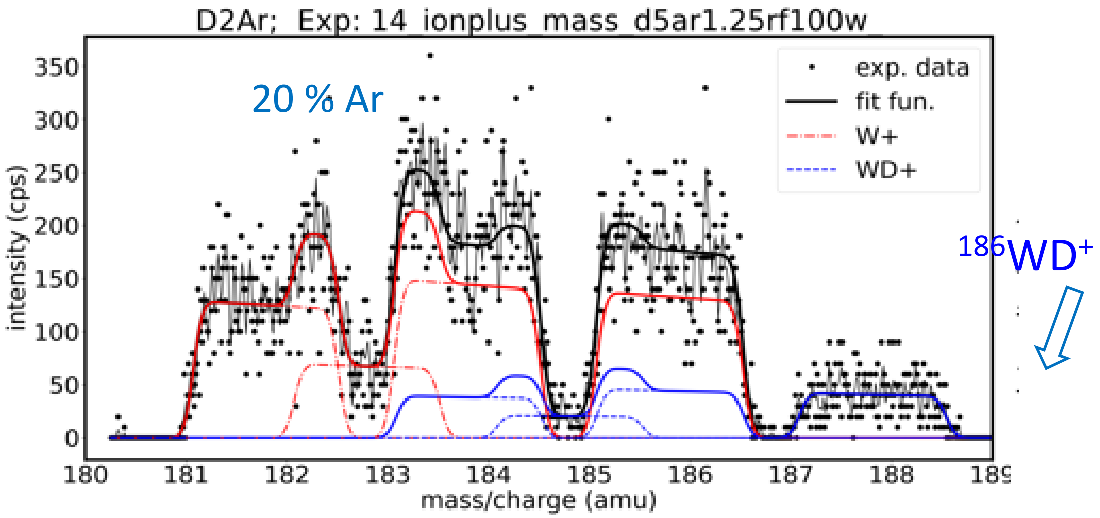


Lesson: In Hydrogen (Deuterium) dominated discharges injected with Ar the sputtering process is sustained by ArH^+

T. Acsente et al. **2024** *Plasma Chem. Plasma Proc*. (https://doi.org/10.1007/s11090-024-10499-z)

W^+ zone: Evidence for WH and WD species in sputtering H_2 (D_2) plasmas





Identified species: W^+, WH^+, WD^+

Development of a fitting procedure

C. Craciun et al., Molecules 2023, 28, 5664, 28155664 (https://doi.org/10.3390/molecules)

Fitting the W^+ region

Two contributions in signal, each with 4 components:

1) assignable to W^+ peaks,
2) assignable to WH^+ species.

please notice that it is similar for WD^+:

G. Dinescu et al., Molecules **2024**, 29(15), 3539

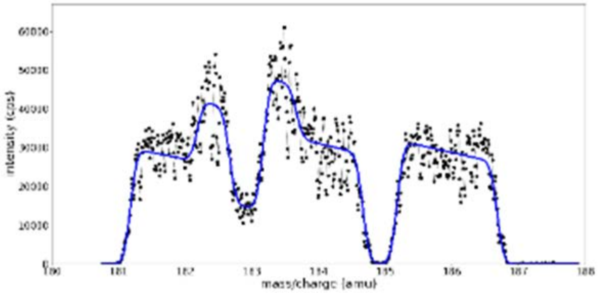
WD detected in Tokamak (OES):

ASDEX, TEXTOR: S. Brezinsek et al. **2019**, *Nuclear Materials and Energy*, vol. 18, pp. 50-55,

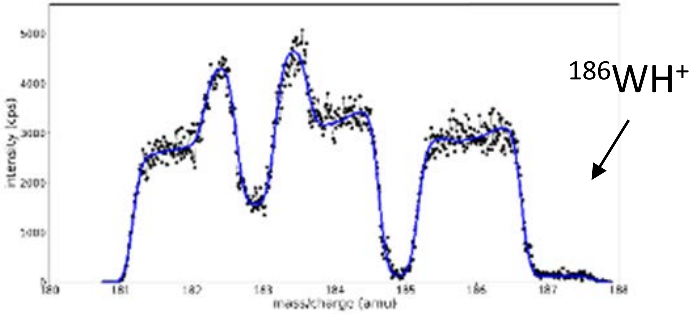
EAST: *Q. Zhang et al. Nuclear Materials and Energy,* **2022,** vol. 33, p. 101265,.

Is the WH^+ percentage significant?

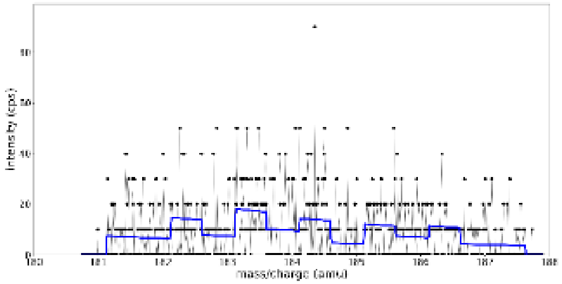
H_2 = 0%
(Ar only)



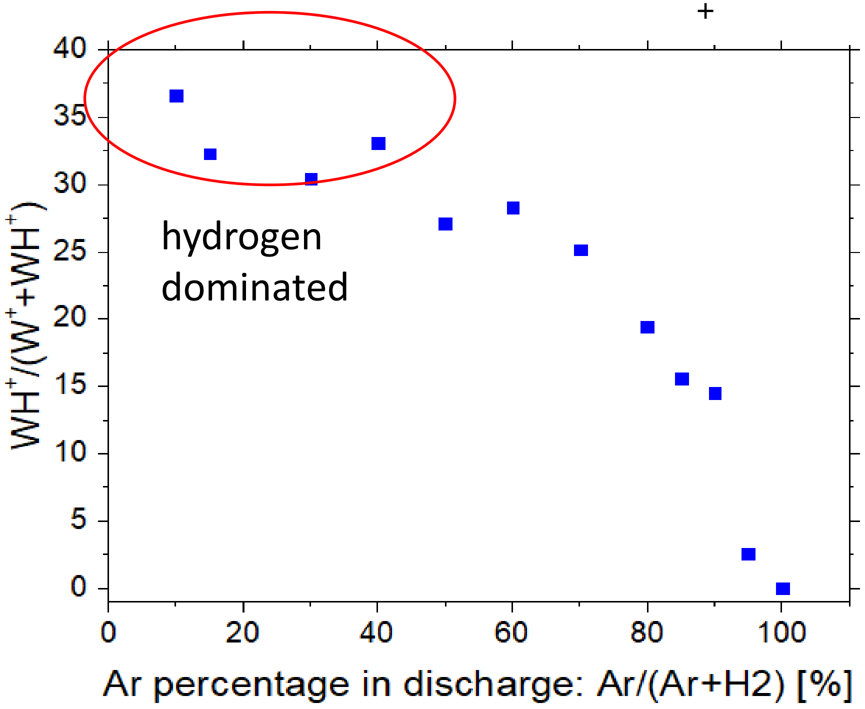
H_2 = 5%
Ar =95%



H_2 = 90%
Ar = 10%



Evaluation of the ratio $\frac{WH^+}{W^+ + WH^+}$

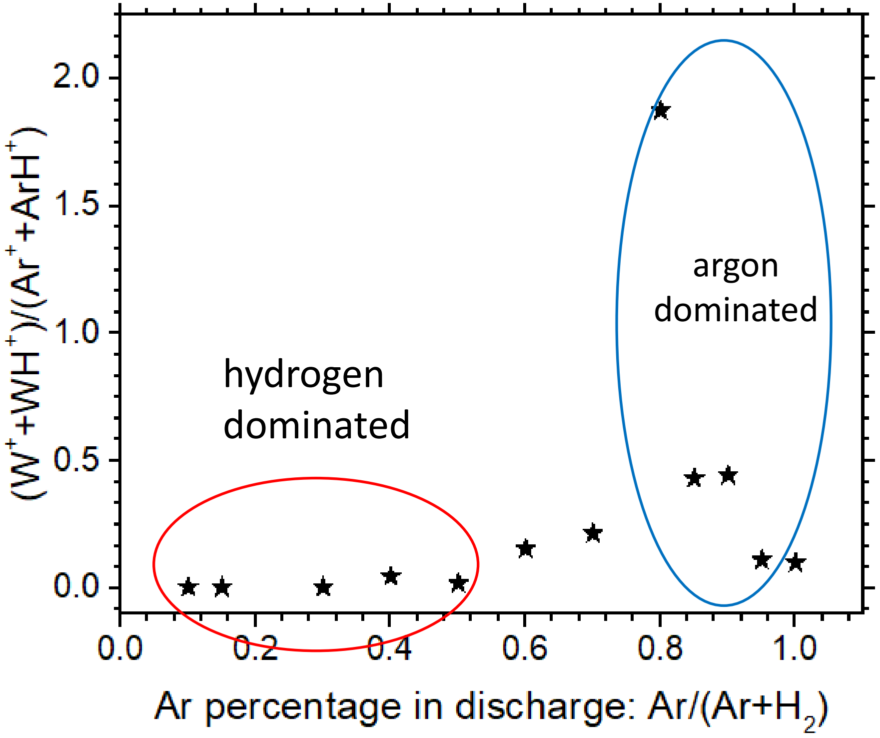


Lesson: Not-negligible WH^+ percentages:
$WH^+/(W^+ + WH^+)$ ~30 - 40 % for gas ratios
$Ar/(Ar+H_2)$ ~ 10-20%

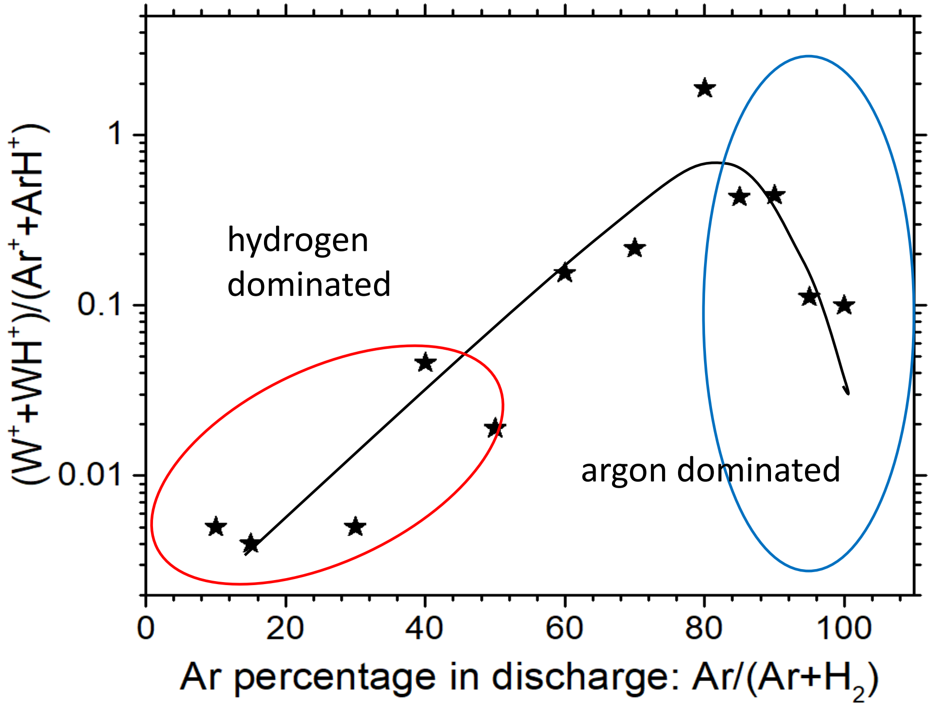
Rough evaluation of the behavior of the sputtering rate

Ratio of the number of W species found in plasma per number of incident sputtering ions ~ $\frac{W^+ + WH^+}{Ar^+ + ArH^+}$ roughly describe the sputtering rate

linear Oy scale



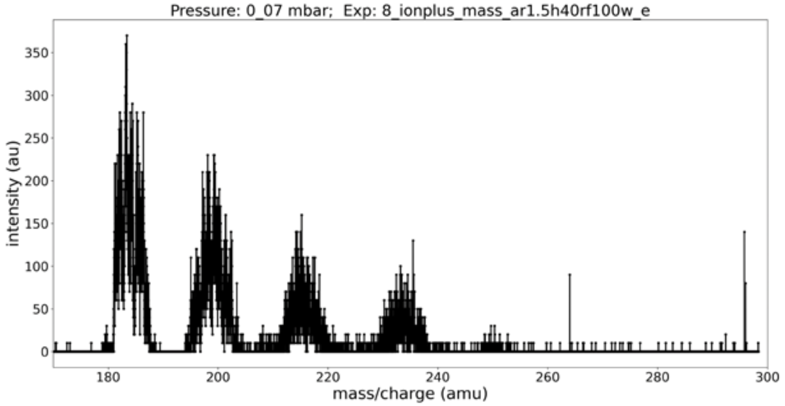
logarithmic Oy scale



- Lesson: Hydrogen dominated discharges: the sputtering rate increases with Ar content

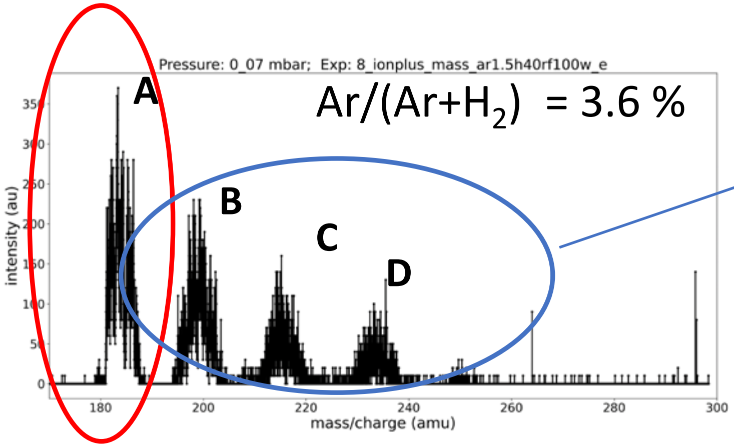
It will be used latter in discussion!

The noisy region 200-250 amu: assignment of peaks to species



S. D. Stoica et al., Plasma Process Polym. **2024**, e2300227 (https://doi.org/10.1002/ppap.202300227)
G. Dinescu et al., Molecules **2024**, 29(15), 3539 (https://doi.org/10.3390/molecules29153539

W species in sputtering H_2(D_2) -dominated plasma: mass spectrometry

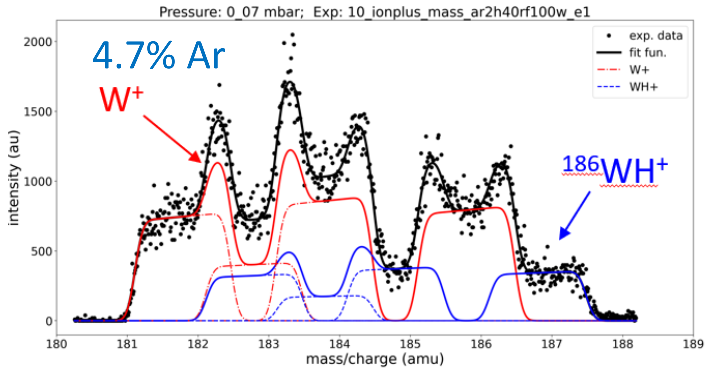


Which is the origin of the group of peaks: B,. C, D...

Experimentally observed that the B,C,D... peaks :

- increase by increased Ar in H_2 discharge
- increase by adding O_2 in discharge
- increase by adding N_2 in discharge

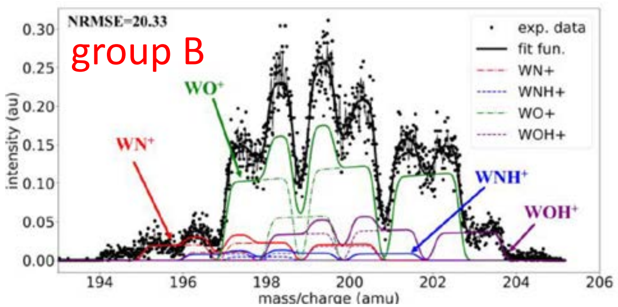
group A : clearly assigned to W, WH^+ peaks

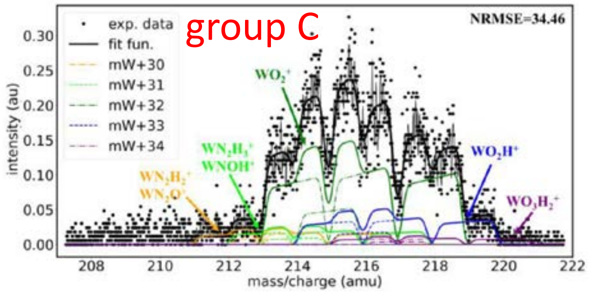


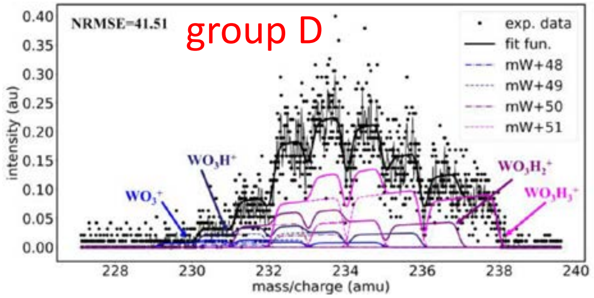
Hypothesis: chemical combinations of one W atom with impurity O, N, H (or D) atoms; we injected O_2 and N_2 gases to confirm

Evidence for $WO_xN_yD_zH_t^+$ molecular tungsten species in hydrogen (deuterium) plasmas with O_2, N_2 impurities in contact with W surfaces

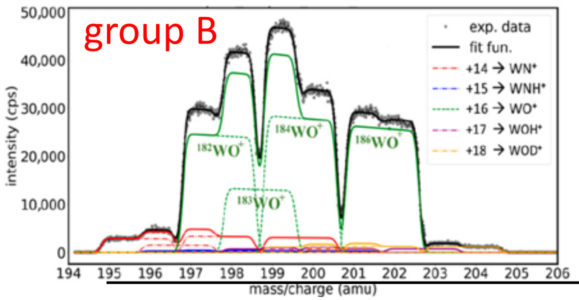
$W/H_2/Ar$ + impurities

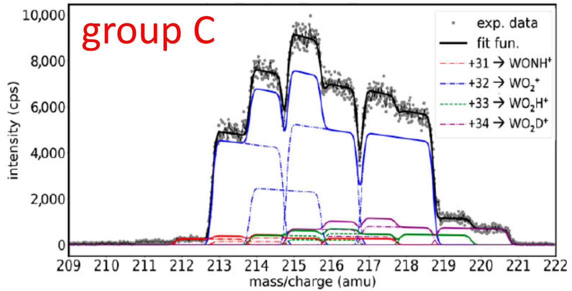


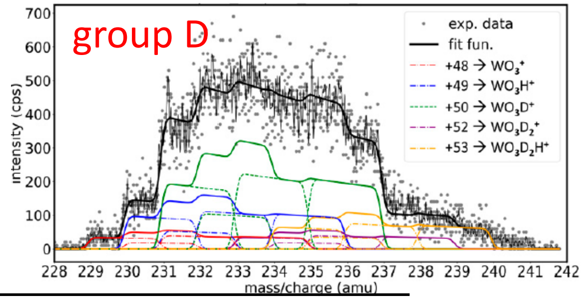




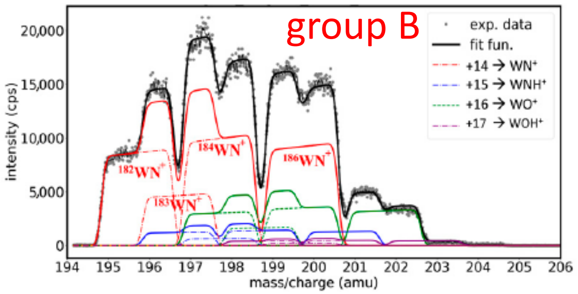
$W/D_2/Ar + O_2$

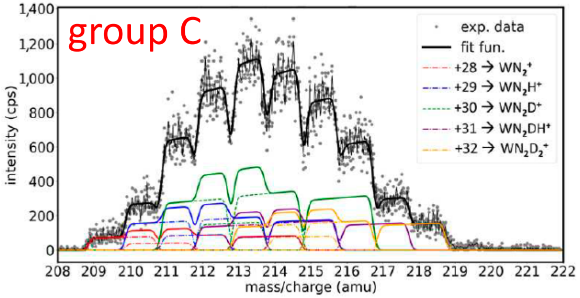


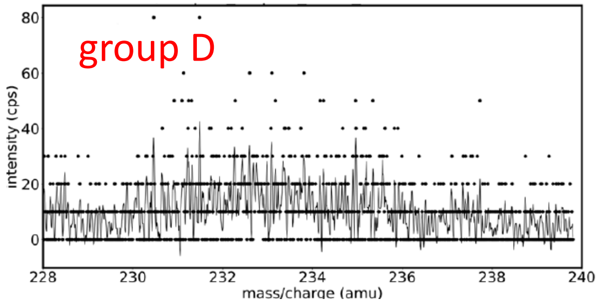




$W/D_2/Ar + N_2$





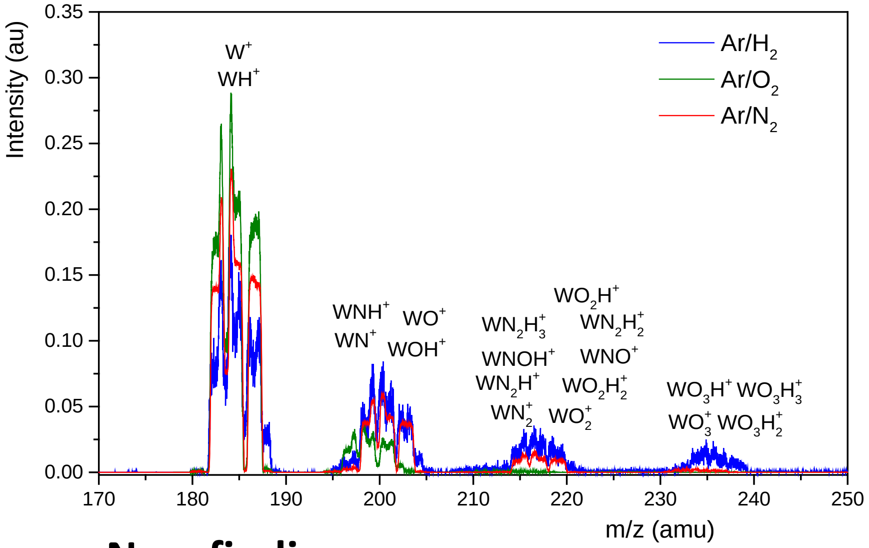


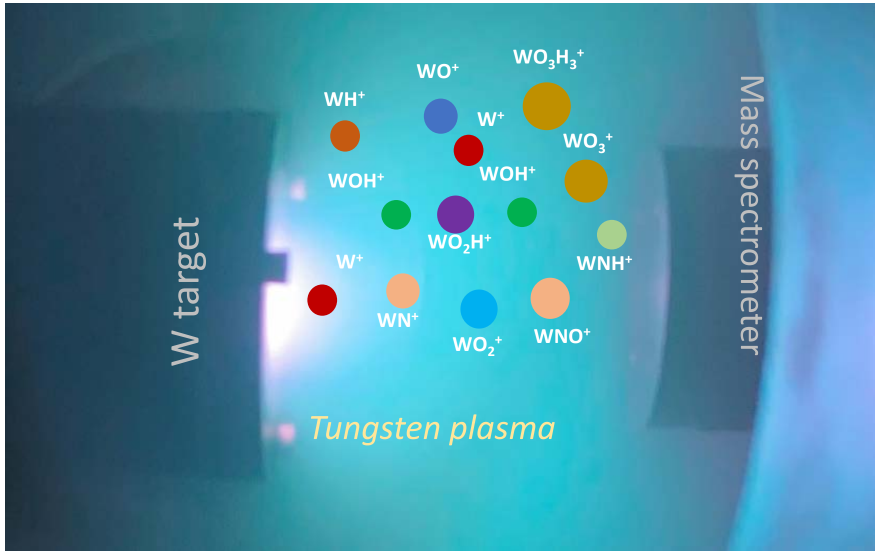
WO^+, WOH^+, WN^+, WOD^+, WND^+, $WNHD^+$

WO_2^+, WO_2H^+, WO_2D^+, WN_2^+, WN_2H^+, WN_2D^+, WN_2DH^+, $WN_2D_2^+$

WO_3^+, WO_3H^+, $WO_3H_2^+$, $WO_3H_3^+$, WO3D+, WO_3DD_2+, $WO_3D_2H^+$, $WN_3H_xD_y^+$ is in noise)

Lessons learned from plasma investigation of hydrogen (deuterium) dominated sputtering plasmas in contact with W surfaces





New findings:

- The material released from the W surface is found not only as W atoms, but also as tungsten molecular compounds formed in reactions with H2(D2), O2, and N2 gas;
- In W/H_2/Ar plasma the species identified in the mass range 180-250 amu and can be described by the general formula $WO_xN_yH_z$ (x=0-3; y=0-3; z=0-3).
  S. D. Stoica et al., Plasma Process Polym. **2024**, e2300227
- In W/D_2/Ar plasma the species identified in the mass range 180-250 amu and can be described by the general formula $WO_xN_yD_zH_t$ (x =0–4, y=0–3, z=0–3, t=0–5.).
  G. Dinescu et al., Molecules **2024**, 29(15), 3539

Raised questions, problems that might be approached:

- Are the molecular W species formed in volume (association reactions) or ejected from surface (sputtering, sublimation)?

- Are the new detected molecular species involved in the nucleation process?

- Is there instrumentation/interest in the community to detect larger mass molecular species containing more than one W atom? (WnOxNyDzHt, with n=2,3,4... – a mass spectrometer in the range 0-1000 amu is needed)

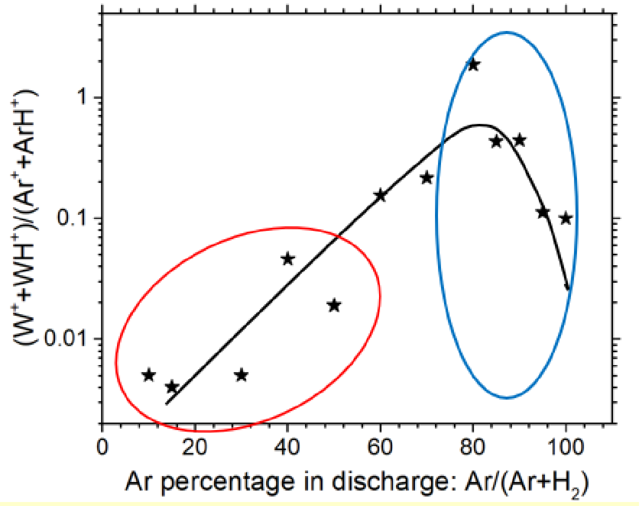
- Are there existing and are tools and interest to detect such species in Tokamak?

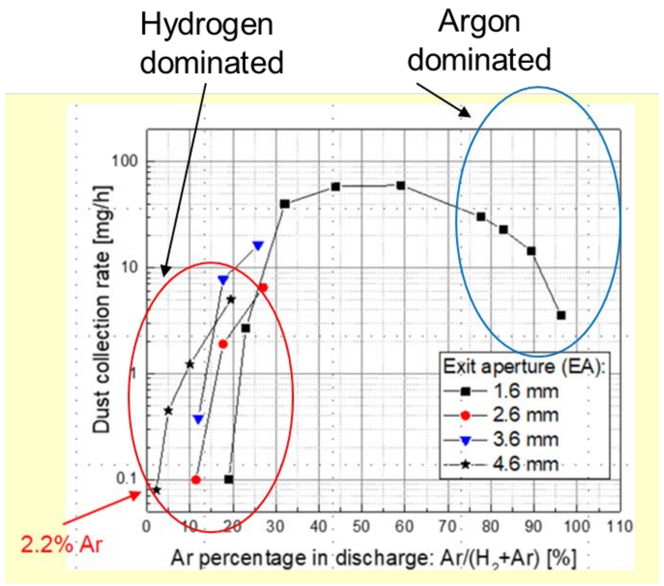
- How the molecular species ($WO_xN_yH_z$, $WO_xN_yD_zH_t$) influence the presently known balance of W material in Tokamak ?

Insights into dust formation mechanisms

Hydrogen plasmas in contact with tungsten
surfaces in presence of small percentages of Kr

How species transform to dust: an experimental journey in the mechanism of dust formation





SPECIES

nucleation

growth

DUST

Mechanisms of dust formation, questions:

Is dust formed at surface?

Is dust formed in volume?

Micron size dust can be formed?

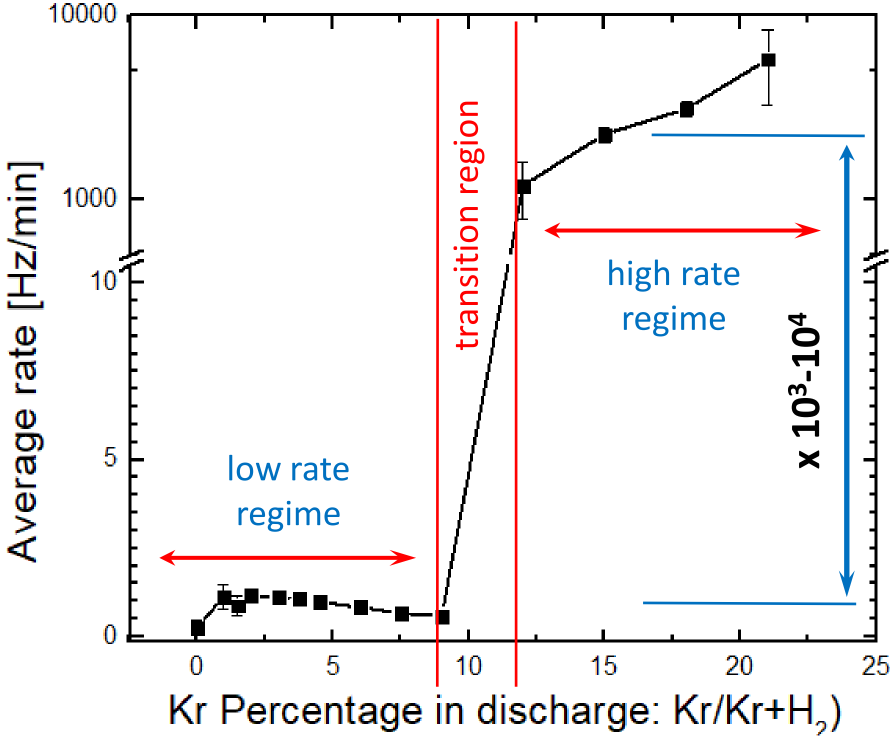
Experiments for answering:

- Quartz crystal microbalance (QCM) for determining mass –
- used simultaneously with SEM to observe the dust.
- Experiments in H_2 injected with Kr!

Dust formation rates upon the injected gas percentage

QCM results: Kr injected in H_2 plasma

Experimental details: MSGA system,
Sputtering power=100 W, p=0.07 mbar,
gas ratios $Kr/(H_2+Kr)$ = 0 - 22 %



Dependence of mass rate upon Kr/(H$_2$+Kr) gas ratio (average upon 3 independent measurements)

Remarks:

-at Kr percentages less than ~10% the dust collection rates are very low (QCM frequency variations ~1Hz/min) - low rate regime;

-at Kr percentages higher than ~15% the dust collection rates are extremely high (10^3-10^4 Hz/ min) – high rate regime;

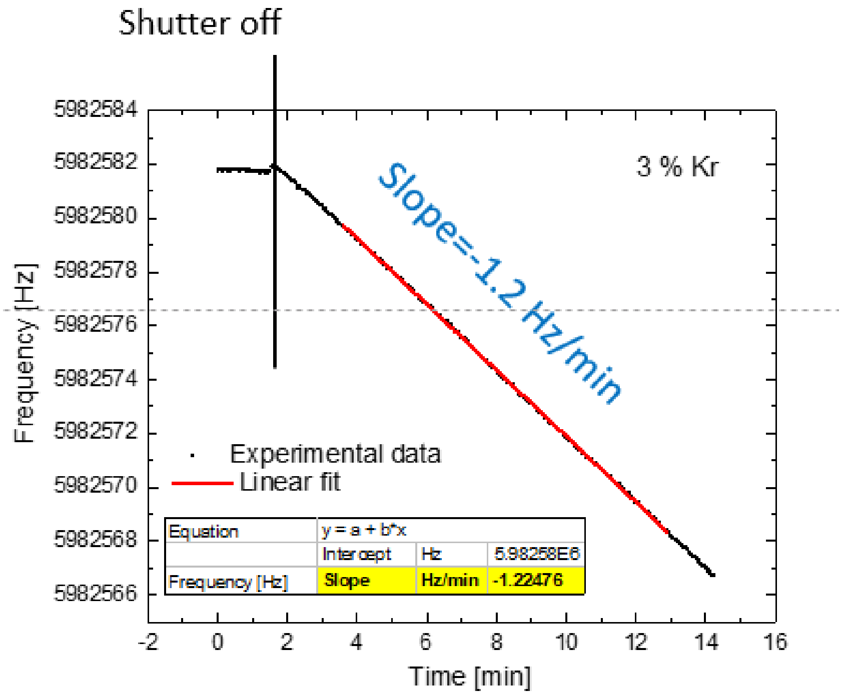
- there is a transition region in the process, associated with a critical Kr percentage in the range 8-13%; once exceeded the critical value **explosive increase (10^3-10^4 times)** of dust production rate is observed.

Conclusion: There is a critical value of Kr percentage leading to explosive increase of dust formation rate

Low rate regime – dust collection rate versus dust morphology

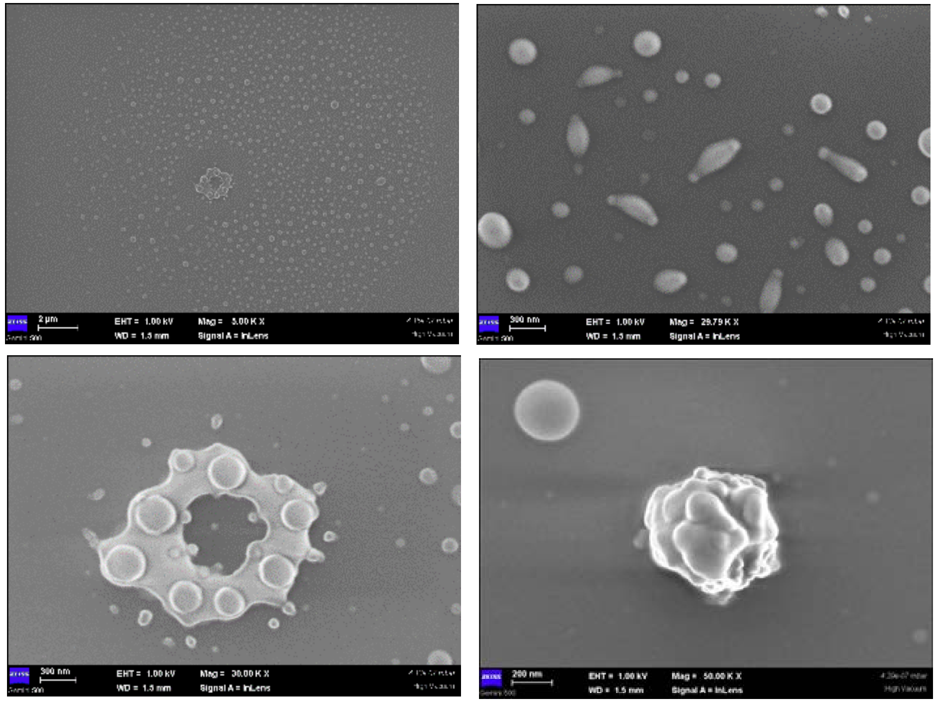
Low rate regime (3%Kr)

MSGA system,
Sputtering power=100 W, p=0.07 mbar,
gas ratios Kr/(H_2+Kr) = 3 %



Equation	y = a + b*x		
	Intercept	Hz	5.98258E6
Frequency [Hz]	Slope	Hz/min	-1.22476

Images of collected dust, collecting time: 3 h



- Many nanometric particles but also of micron size.
- The nanoparticles surround the big particles;
- Some of nanoparticle seems melted;
- High-size particles made from many fused nanoparticles

QCM rate : Continuous mass increase

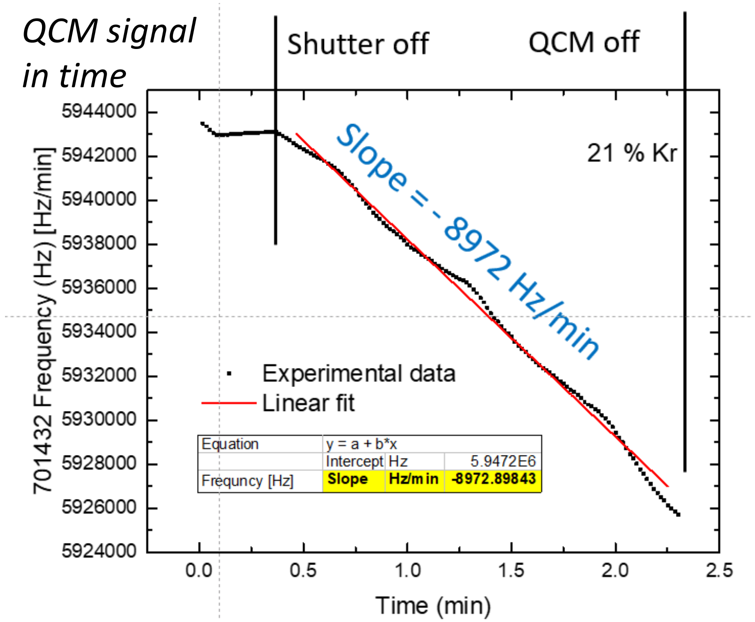
Dust aspect: Discontinuous and non-uniform coverage

Contradiction: QCM indicates a continuous increase of mass on substrate; SEM indicates discontinuous surface coverage, big particles, even micron size!

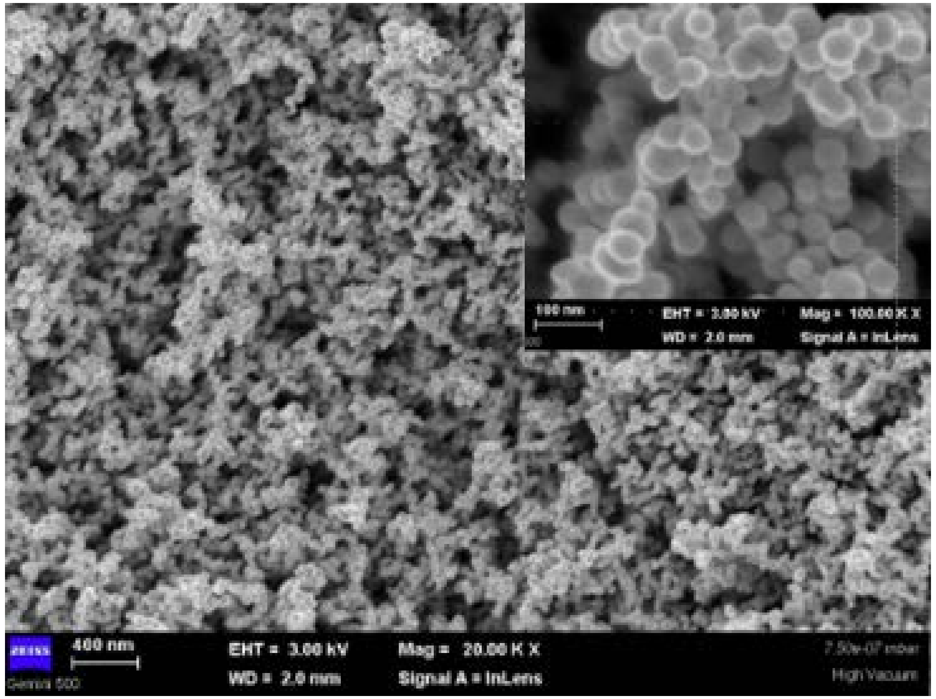
High rate regime – dust collection rate versus dust morphology

High rate regime (21% Kr)

Experimental details:
MSGA system,
Sputtering power=100 W,
p=0.07 mbar,
gas ratios Kr/(H_2+Kr) = 21 %



Dust deposited on the QCM crystal during a high rate deposition (21% Kr)



Individualized, round particles with sizes in the range 50-100 nm are well distinguished.

Continuous mass increase ↔ Dust aspect: uniform, continuous coverage of the substrate with nanoparticles

QCM and SEM results are converging!

Dust growth mechanisms

Low rate regime - Growth by a surface mechanism:

- diffusion of t W atoms on surface and concentration around centres of nucleation;

- formation of small-size clusters and nanoparticles distributed on surface;

- migration on substrate and fusion of clusters and small-size nanoparticles, larger particles formed by coalescence;

- larger particles keep increasing in size ending eventually in a reduced number of large particles, even of micron size. – sputtering can lead to micron size dust

High rate regime - Growth by a volume mechanism:

-high concentration of W species in the gas phase, favours nanoparticle formation by volume nucleation and growth by atom addition;

-volume processes prevail on surface processes and particles formed in volume are collected; -

Lesson learned: with increasing sputtering rate a **critical value of the W species concentration** in plasma is reached, when the mechanism of particle formation switches from surface processes, to volume processes!

Question raised, problems that might be approached:

- How the surface growth mechanism behaves on W surfaces?
- How to determine the critical density of species, leading to the switch of the growth mechanism?
- How compare the dust formation rates for the gases used for detachment, in the series Ne, Ar, Kr ?

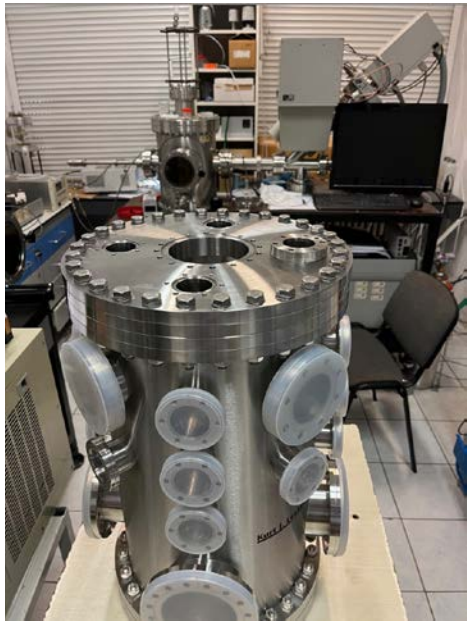
- Is a similar research of interest for boronized surfaces ! ?

PWIE workshop on Plasma-Wall interaction in full W devices,
September 17-19 2024, Aix en Provence, dinescug@infim.ro

Opportunities for further work

New infrastructure for experiments at IAP-INFLPR

- A new MSGA system with extensive diagnostics was designed and is in the configuring stage:
  - dedicated ports for the MSGA source, and diagnostics
  - QCM thermalized within 0.01 °C stabilization
  - scattering laser diagnostics for detecting nanometric dust
  - camera for dust visualization
  - allows for dust coating of large surfaces for studies of dust adhesion and mobilization;



- A new RF-PECVD setup with **diborane B_2H_6** as precursor was realized and tested;

- Advanced equipment for dust characterization: SEM, TEM, XPS

Proposed further work

Study of dust formation in plasmas in contact with W, B-W and B surfaces

and, if it is found of interest:

Laboratory studies of W boronization by PECVD processes with diborane as precursor

Advance in modelling of dust growth

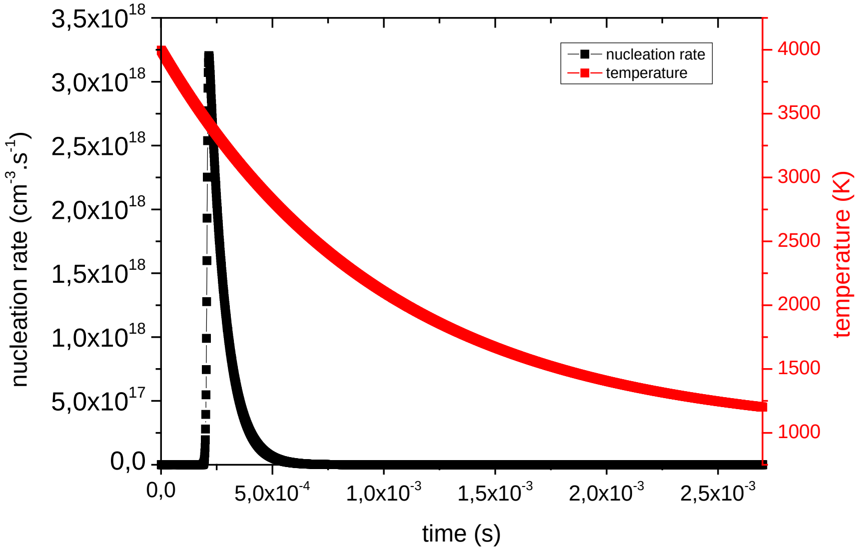
Khaled Hassouni

LSPM, CNRS, Université Paris 13 Sorbonne Paris

Nucleation and growth inside the equilibrium metal vapor after a thermal quench

A thermal quench of the equilibrium tungsten vapor (that may be produced or that surround a tungsten droplet emitted after after anomalous event) is simulated and the nucleation inside the vapor is investigated – Simulation conditions : T_0 4000 K, t_{quench} =1 ms

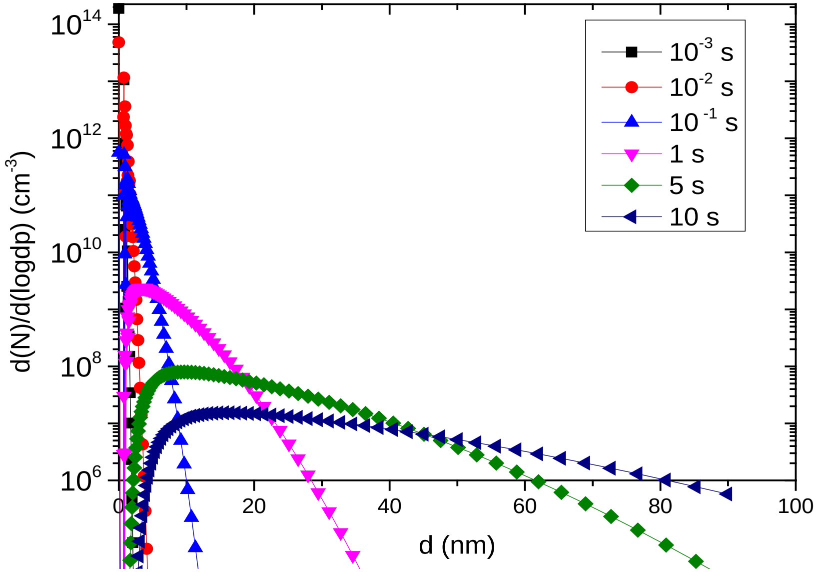
Nucleation rate and temperature variation during the thermal quench



➔ Nucleation delay: to reach the critical supersaturation

➔ Nucleation burst

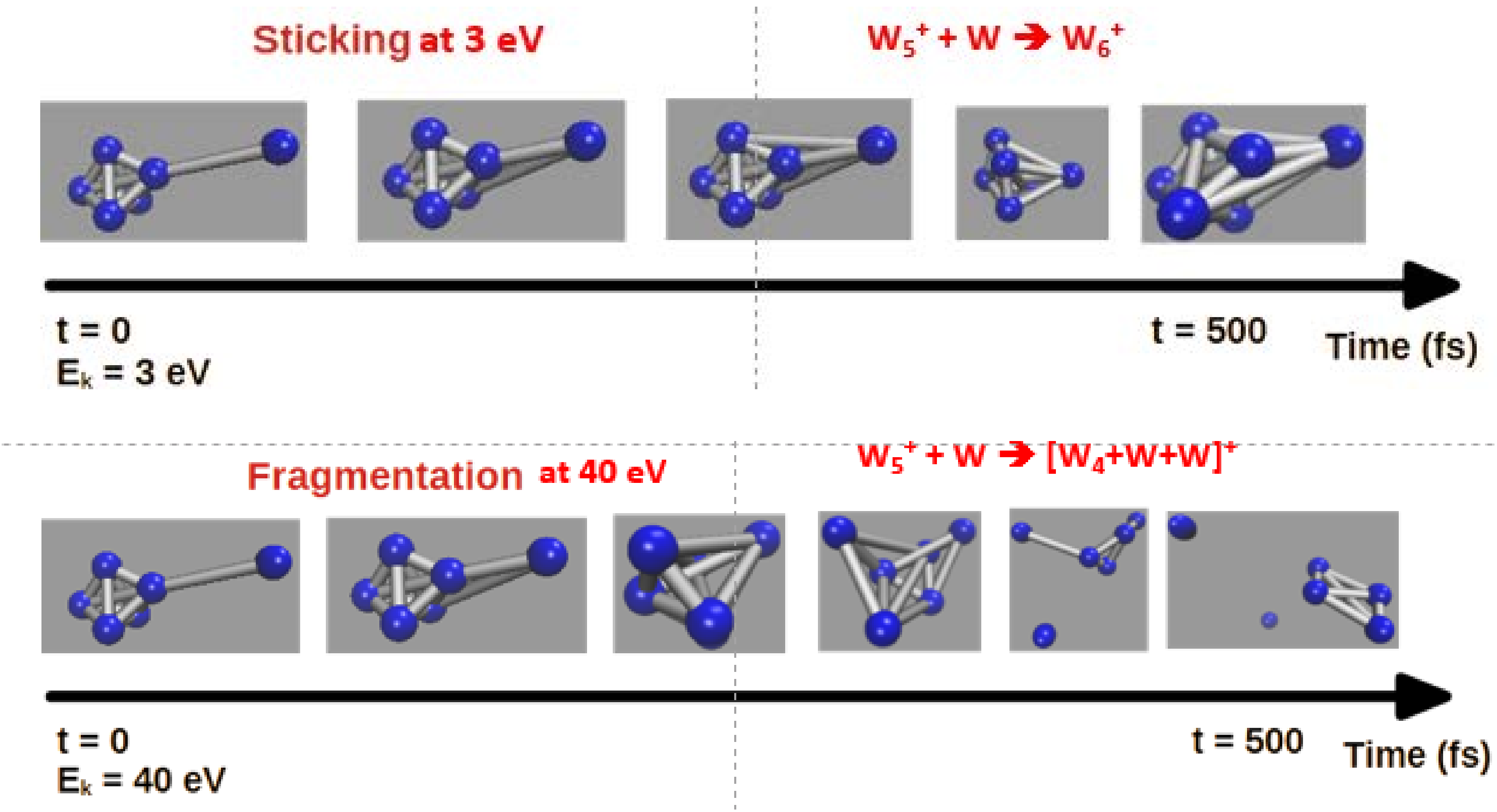
Particle size distribtution evolutions after the nucleation burst



Coagulation ➔ decrease of the nucleus population ➔ formation of larger particles and a wide particle size-distribution

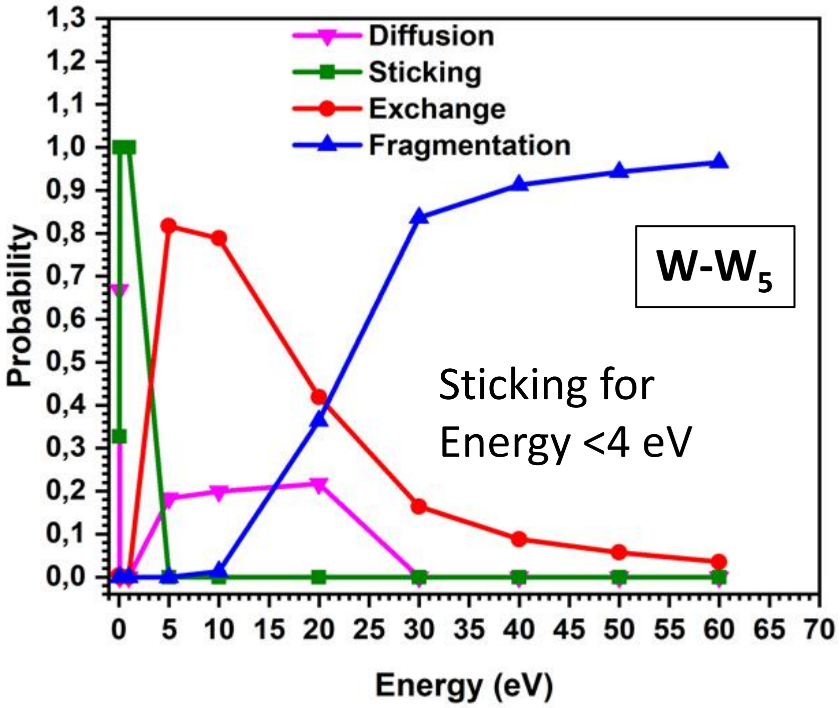
Ab initio MD of collision between charged tungsten clusters and W atom -

Case of W_5^+

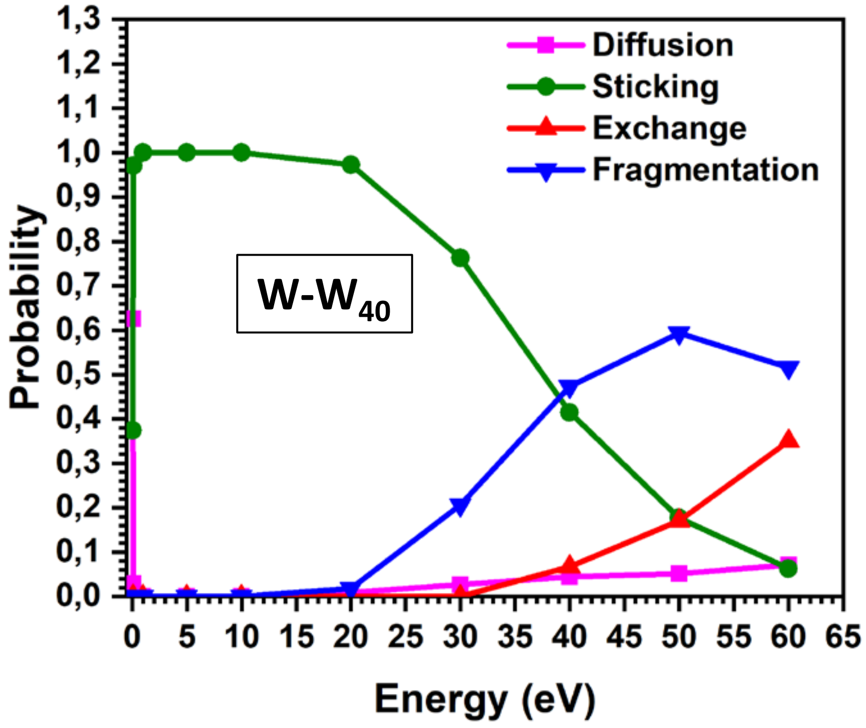


Collision energy is important for sticking or fragmentation

Sticking probability as a function of collision energy during cluster-atom collisions



Sticking for
Energy <4 eV



1- Sticking and growth is favored by increasing size ➔ the small clusters are less prone to remain in life

2- For $W_{40,}$ sticking is almost the only process taking place for Energy <20-25 eV

Thank you for your patience !