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Gas Phase Synthesis of Nanoclusters and Nanoalloys

April 28, 2022, Cargèse, Corsica
Spring school on nanoalloys: from structure, kinetics and environment to properties and applications

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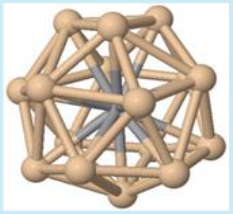
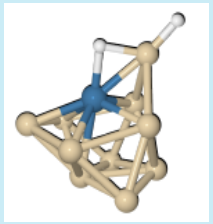
My research

Free clusters



geometry $Si_{16}V$ [1]

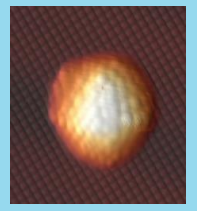


reactivity $Al_{10}V^{+}+H_2$ [2]

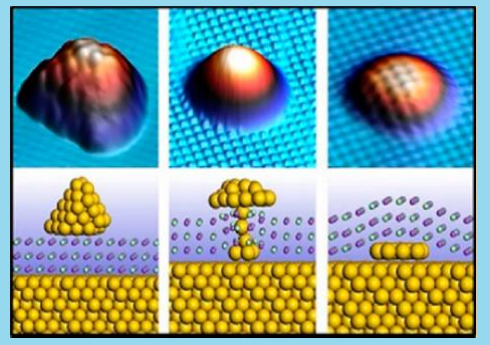
- Intrinsic, size-dependent, non-scalable properties of few-atom clusters
- Correlation geometry, electronic structure, magnetism, chemical reactivity…

Deposited clusters

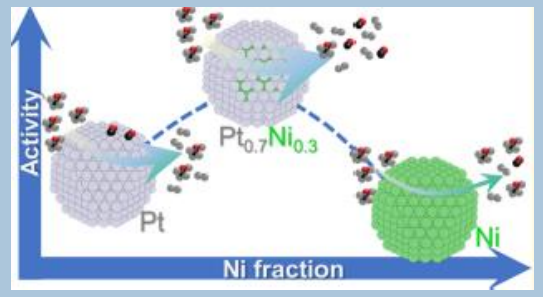
- Cluster-support interaction
- Structural and electronic investigation STM/STS



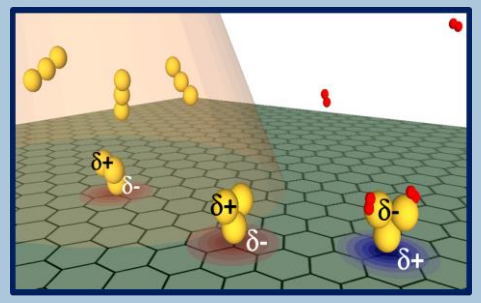
Co cluster on NaCl [3]



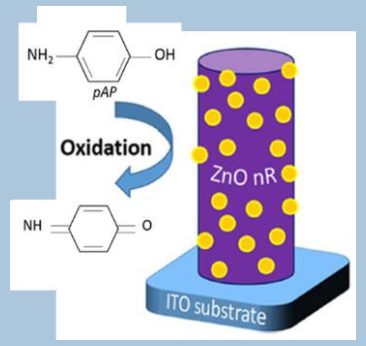
Size-dependent Au cluster penetration through NaCl [4]



Pt_xNi_{1-x} catalysts for methanol dehydrogenation [5]



Au_3/graphene devices [6]



cluster decorated nanorods as sensor material [7]

Clusters for catalysis, sensors, electronic devices

[1] Claes *et al*, PRL **107**, 173401 (2011); [2] Ferrari *et al*, Acc. Chem. Res. **51**, 3174 (2018);
[3] Schouteden *et al*, Nanoscale **6**, 2170 (2014]; [4] Li *et al,* Nano Lett. **16**, 3063 (2016); [5] Liao *et al*, Chem. Mater. **31**, 10040 (2019),
[6] Scheerder *et al*., Nanoscale **9**, 10494 (2017); [7] Fiaschi *et al*, J. Electroanal. Chem. **811**, 89 (2018)

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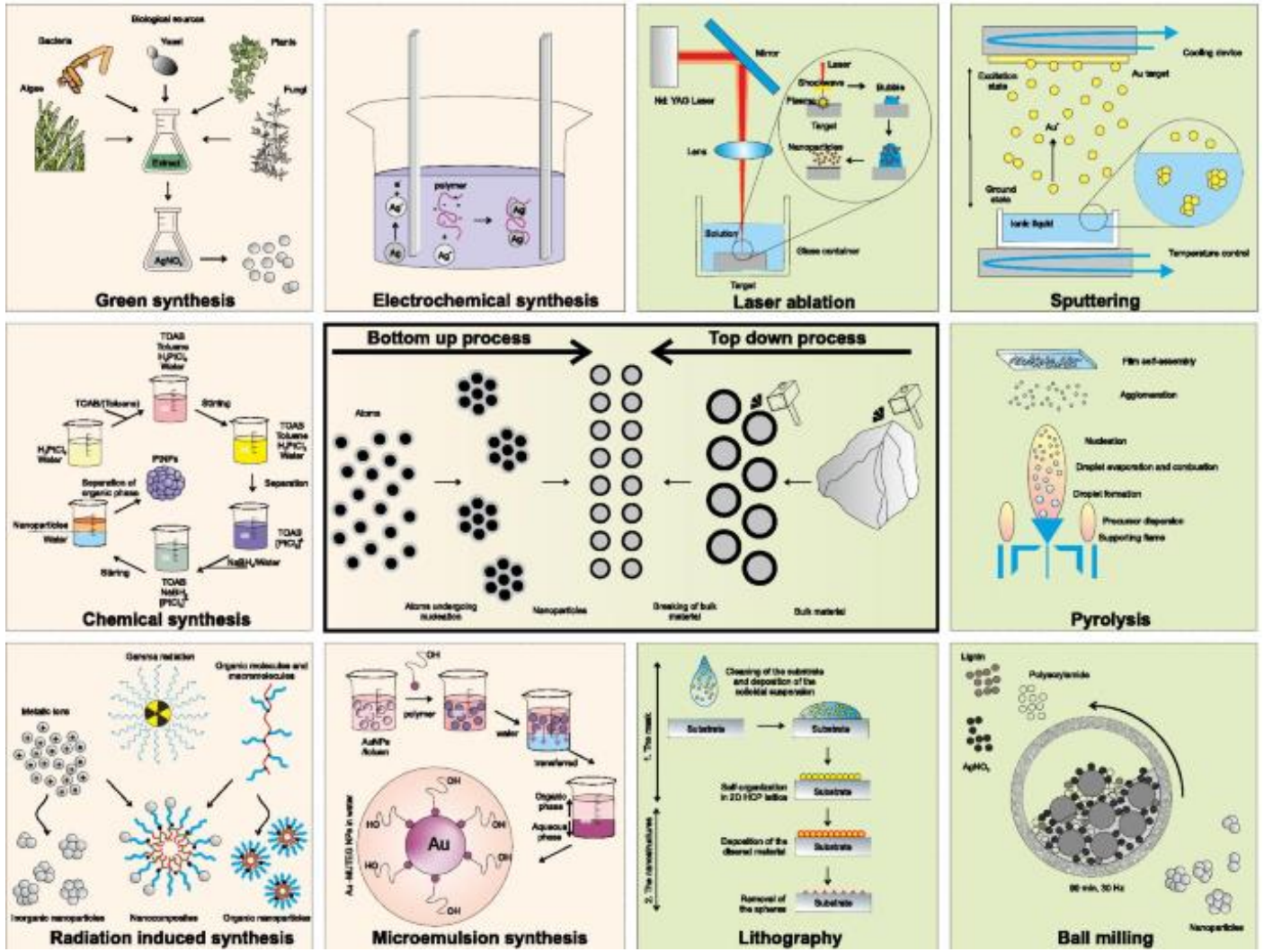
Outline Lecture

1) **General principles** of nanoparticle formation by gas phase aggregation
2) Influence of **source parameters** on the nanoparticle formation process
3) Growth of **nano-alloys** and out-of-equilibrium morphologies
4) **Scaling up** the production
5) **After production:** ion guiding, deposition, temperature in a cluster beam

Nanoparticle growth strategies



Synthesis of NPs in liquids

+ reproducible, up-scalable, cheap, well-established
- surfactants/ligands, structural control due to thermodynamic restrictions

Gas phase synthesis of NPs

+ possible to make particles that cannot be made by other means (out-of-equilibrium morphologies / particles of non-miscible materials), high control (size, composition), high purity ‘naked’ particles, fabrication independent from substrate
- expensive equipment, low yield, not well understood

Source figure: G. Habibullah, J. Viktorova, T. Ruml, *Current Strategies for Noble Metal Nanoparticle Synthesis* Nanoscale Res. Lett. **16**, 47 (2021)

Types of gas aggregation sources

Common aspects

- ✓ **Evaporation of atoms** from pure or alloy bulk materials. This can be done by Joule heating, a flame, ion sputtering, electric discharge, a laser,…
- ✓ Formed vapor is **seeded in an inert gas** to cool down the vapor and initiate **nucleation**.
- ✓ Nucleation is followed by further **growth** (atom per atom) and possible also **coagulation** of larger clusters
- ✓ **Terminated gas condensation** by expansion into vacuum to form a beam of particles. Further cooling (and possibly last growth steps) during the expansion.

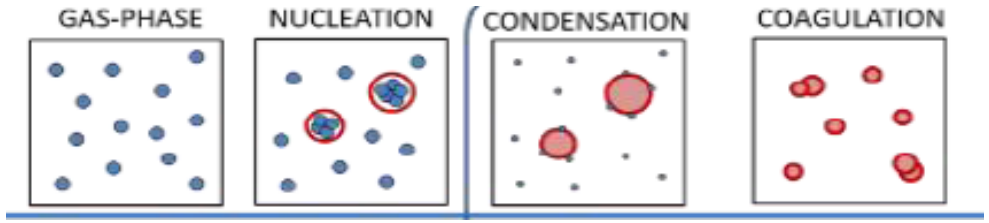
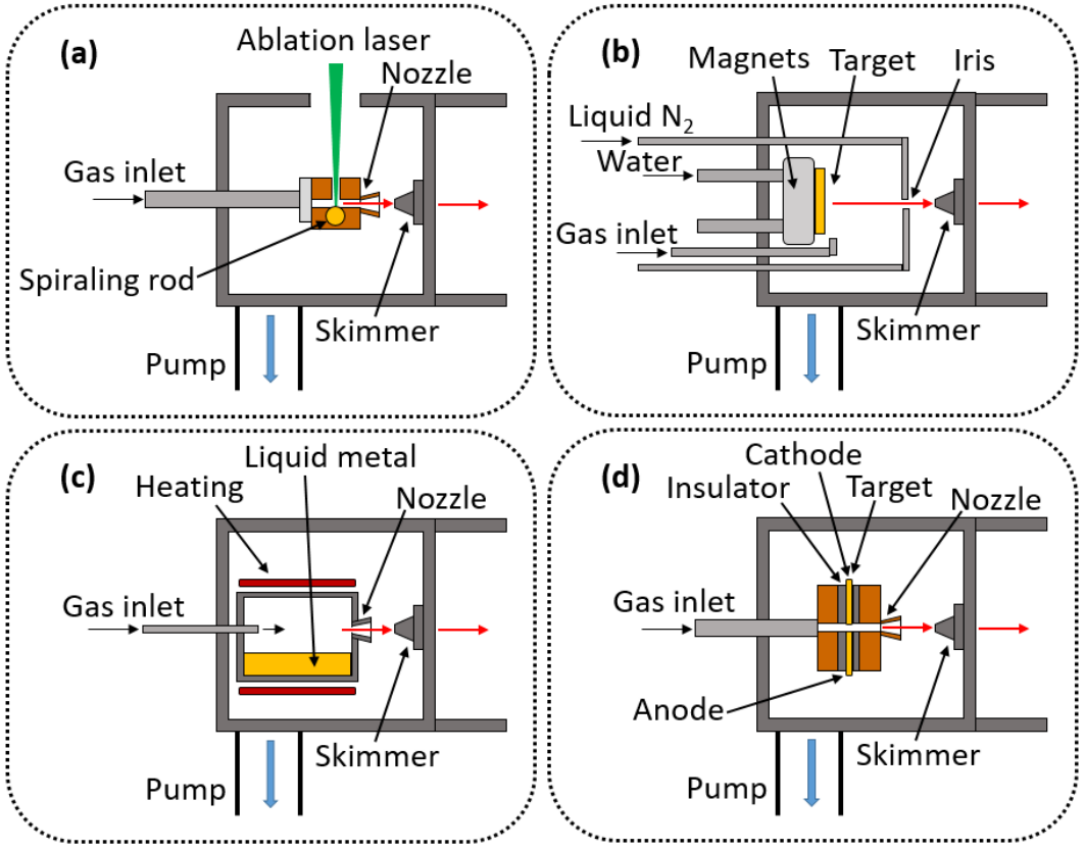


Figure adapted from: F. Strappaveccia, F. Galleni, E. Ghedini, J. Phys.: Conf. Series **1243**, 012018 (2019)



Source figure: P. Ferrari, G. Sanzone, J. Yin, E. Janssens, *Physical synthesis of nanoalloys* in *Nanoalloys: from fundamentals to emergent applications,* editor F. Calvo, Elsevier (2020)

Nucleation kinetics

Probability for nucleation or the formation of germs is determined by the combination of **three elementary reactions** and their corresponding rates (with A and B metal atoms and R a rare gas atom):

Activation: A + B → AB*

Recombination: AB* + R → ….→ AB + R

(collisional) Decomposition: AB* (+R) → A + B (+R)

essential net result:
need for **3-body collisions**
A + B +R → AB + R

Different rates have different dependence on energy/temperature and concentrations of A, B, R.
Microscopic rate coefficient can be approximated by theories as RRKM and detailed balance theories.

The **carrier gas** has three purposes: i) it cariers material out of the source, ii) nucleation requires a high vapour pressure (gas to solid/liquid transition) and iii) takes a way the formation heat. Without removal of the formation heat the particles will quickly fragment.

Example: A + B bind with E_B = 2.5 eV, all energy goes in single vibration mode: 2.5 eV = $k_B \Delta T$ → ΔT = 30.000 K

As soon as particle become larger, it becomes its own heat bath (3N-6 degrees of freedom) and ΔT ↓

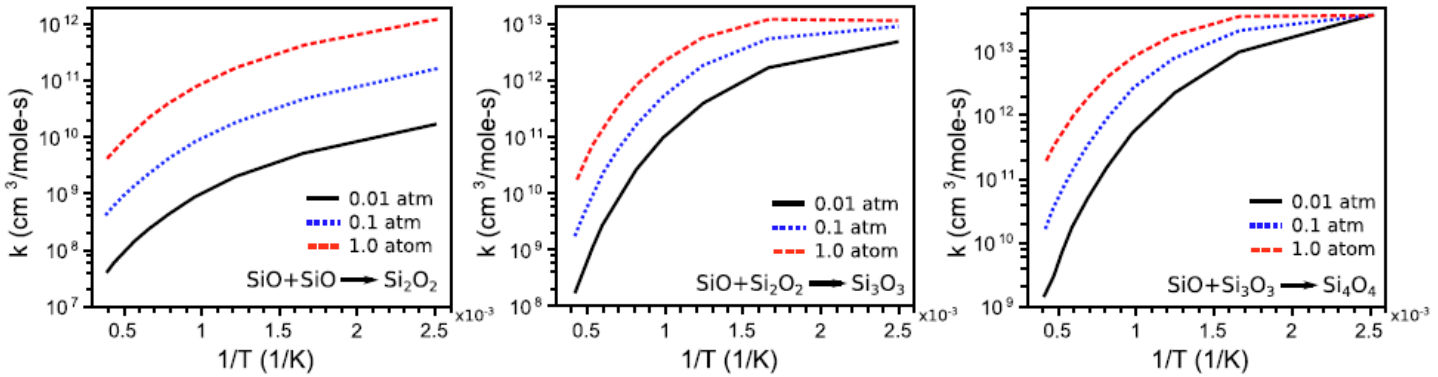
Stable dimer (AB) formation is the most difficult step in the particle formation (actually in some cases other small clusters like trimer could be bottleneck, see J.G. Mattei et al. Chem. Mater. **31**, 2151 (2019)).

Nucleation kinetics

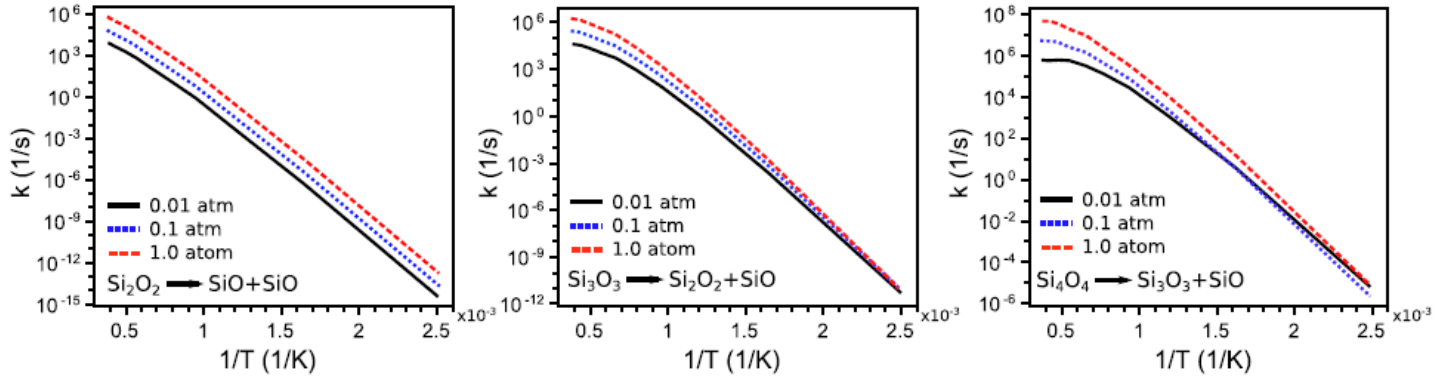
Possible solutions to overcome issue of nucleation barrier:

- High carrier gas pressure
  (but if too high A and B don't meet)
- Dimers already created in evaporation process (true for sputtering)
- Use trace gases / impurities (oxygen, nitrogen,…) for nucleation seeds
  see for example: G. Krishnan et al. Nanoscale **9**, 8149 (2017)

Combined activation and recombination



Dissociation (activated by He collision)



- Formation (dissociation) rate higher (lower) at low temperature.
- Dissociation quite size independent; formation rate small for SiO+SiO
- Higher He pressure increases rates

M.R. Zachariah and W. Tsang, *Application of ab initio molecular orbital and reaction rate theories to nucleation kinetics*, Aerosol Sci. Technol. **19**, 499 (1993)

Growth kinetics

Smoluwkowski model (accounts for **growth** and **coalescence**)

Assumes **irreversible aggregation** (i.e. no dissociation). With n_k the number of clusters of size k and $K_{i,j}$ the aggregation rate between clusters of sizes i and j.

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i+j=k} K_{i,j} n_i n_j - \sum_{i=1}^{\infty} K_{k,i} n_k n_i .$$

Extended Smoluchowski model (accounts also for aggregation with charged particles – indicated with prime; m_k is number of charged clusters of size k)

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i+j=k} K_{i,j} n_i n_j - \sum_{i=1}^{\infty} K_{k,i} n_k n_i - \sum_{i=1}^{\infty} K'_{k,i} n_k m_i ,$$

$$\frac{dm_k}{dt} = \sum_{i+j=k} K'_{i,j} m_i n_j - \sum_{i=1}^{\infty} K'_{k,i} m_k n_i ,$$

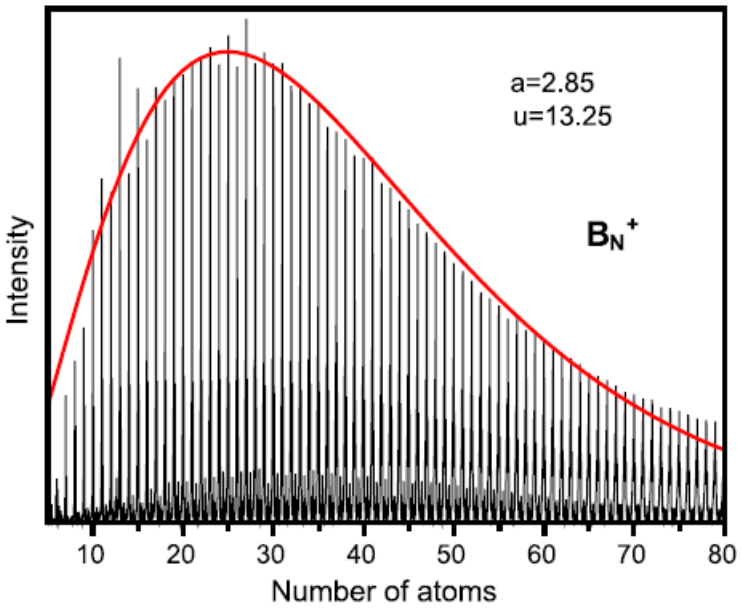
Growth kinetics

Extended Smoluchowski model (accounts for **growth** and **coalescence**)

Solution of model for most trivial assumption that $K_{i,j}$ and $K'_{i,j}$ do not depend on i and j

$$p(k) = \frac{\Gamma(a+k-1)}{\Gamma(a)\Gamma(k)} \frac{u^{k-1}}{(1+u)^k},$$

with $p(k)$ the percentage of charged clusters of size k, $a = 2K'/K$, and $u = Kn_0t/2$, with the time and n_0 the initial number of monomers



P. Ferrari, G. Sanzone, J. Yin, E. Janssens, *Physical synthesis of nanoalloys* in *Nanoalloys: from fundamentals to emergent applications,* editor F. Calvo, Elsevier (2020)

Good fit implies irreversible aggregation and constant K are reasonable assumptions. Collisions with rare gas atoms are needed to stabilize, but this may also imply kinetic trapping (cf. energy barriers for reorganisation, surface diffusion, atomic displacements,…)

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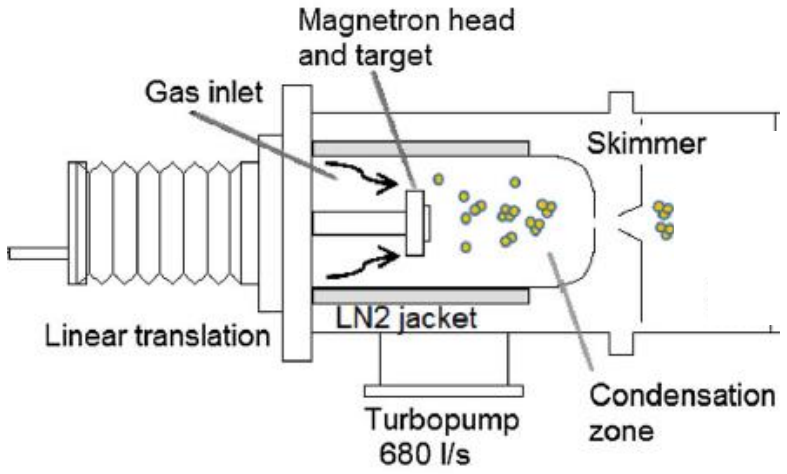
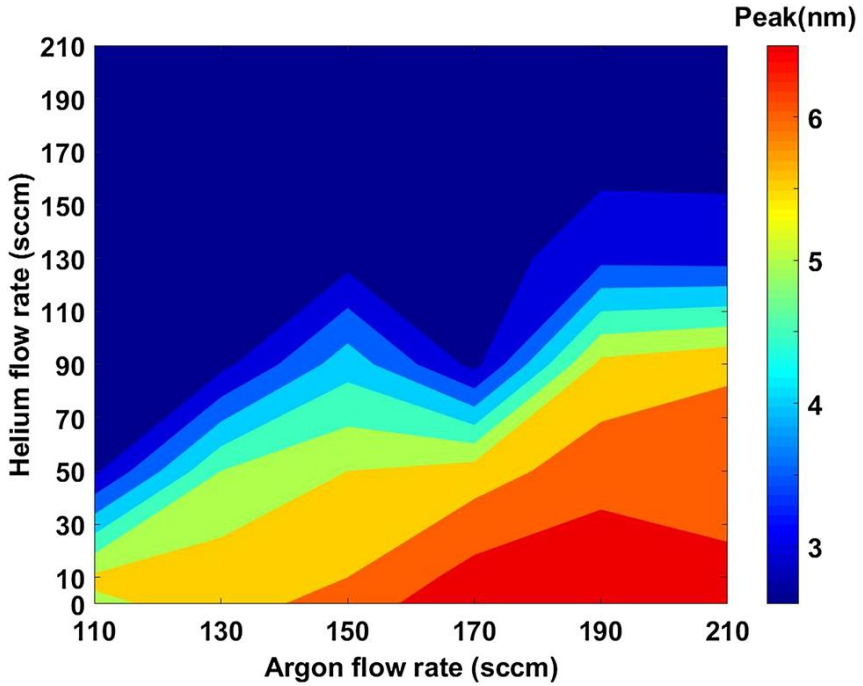
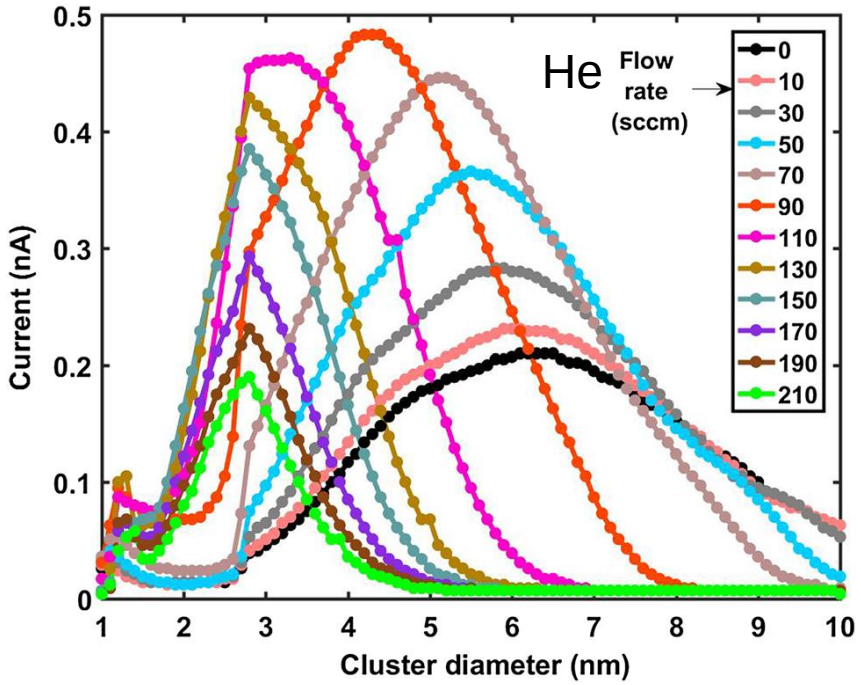
Parameters in a magnetron source



- Observation: for given He flow rate, influence of Ar limited but more Ar leads to larger NPs. With increase He flow rate intensity first increases then decreases and mean particle size is reduced.
- Explanation: Ar more efficient for nucleation and aggregation, while He enhances trapping clusters in gas streamlines (shorter residence time in source).

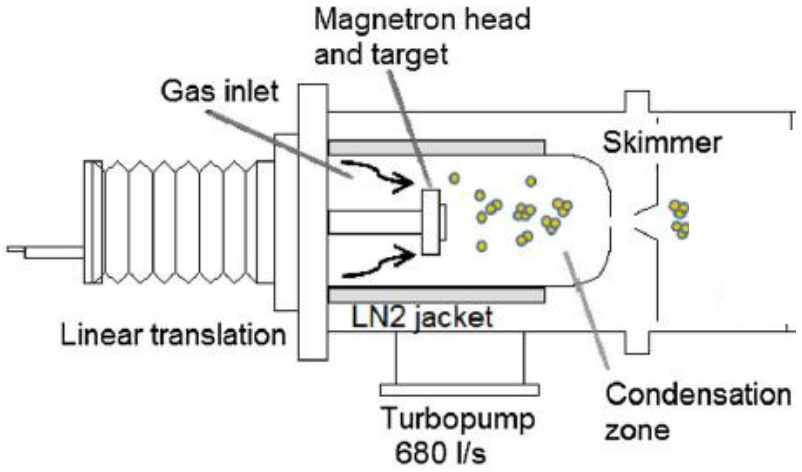
Ar and He flow rates





Source: M. Khojasteh and V. V. Kresin, *Influence of source parameters on the growth of metal nanoparticles by sputter-gas-aggregation*, Appl. Nanosci. **7**, 875 (2017)

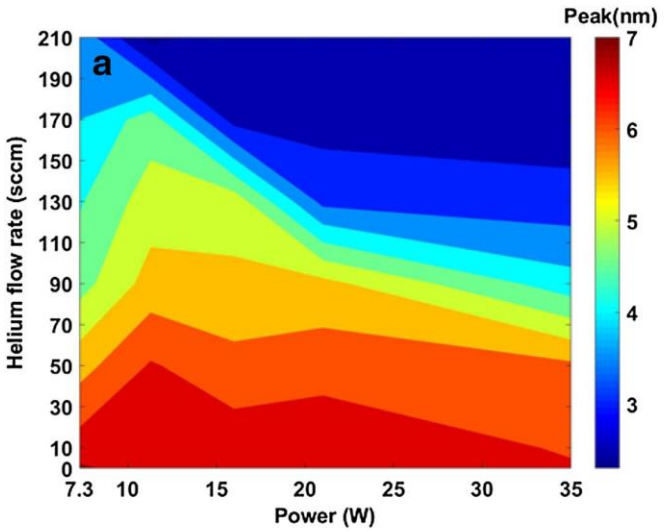
Parameters in a magnetron source

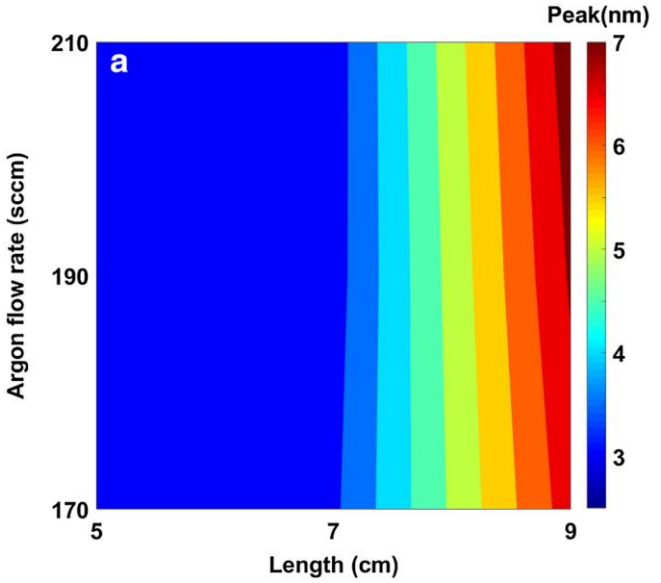


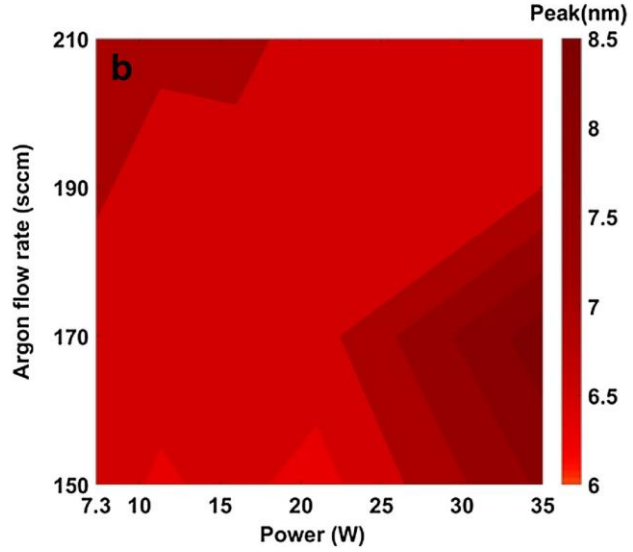
Sputter power and aggregation length

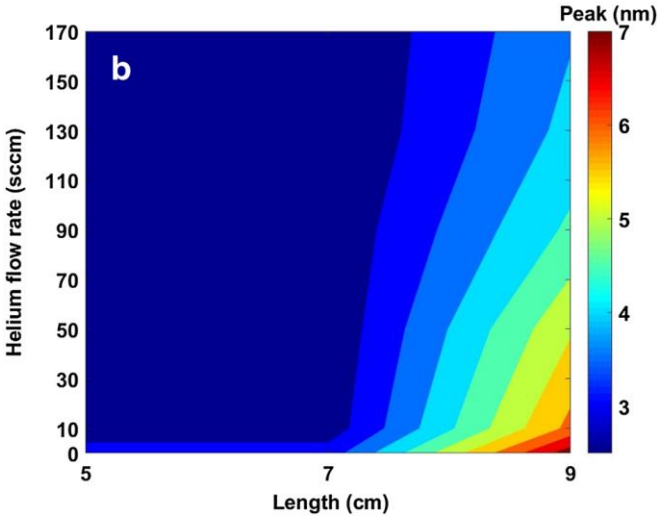
- Higher sputtering power → more material, but there are heat load limitations
- Longer aggregation length → longer growth time (large influence)

Source: M. Khojasteh and V. V. Kresin, *Influence of source parameters on the growth of metal nanoparticles by sputter-gas-aggregation*, Appl. Nanosci. **7**, 875 (2017)



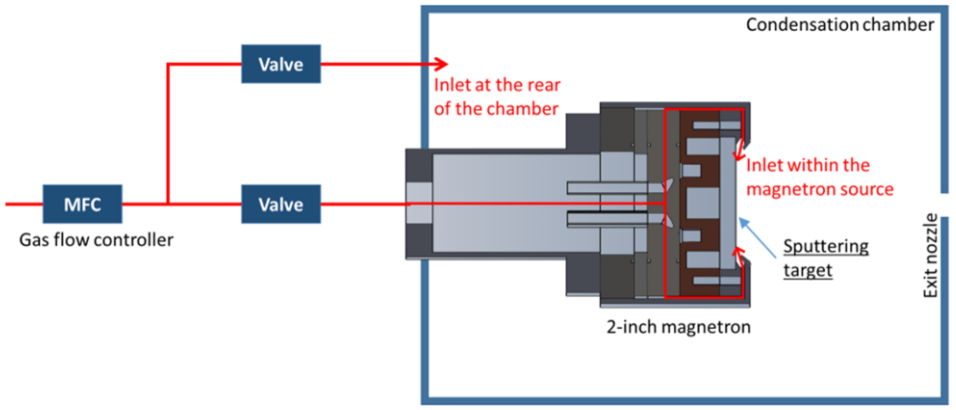


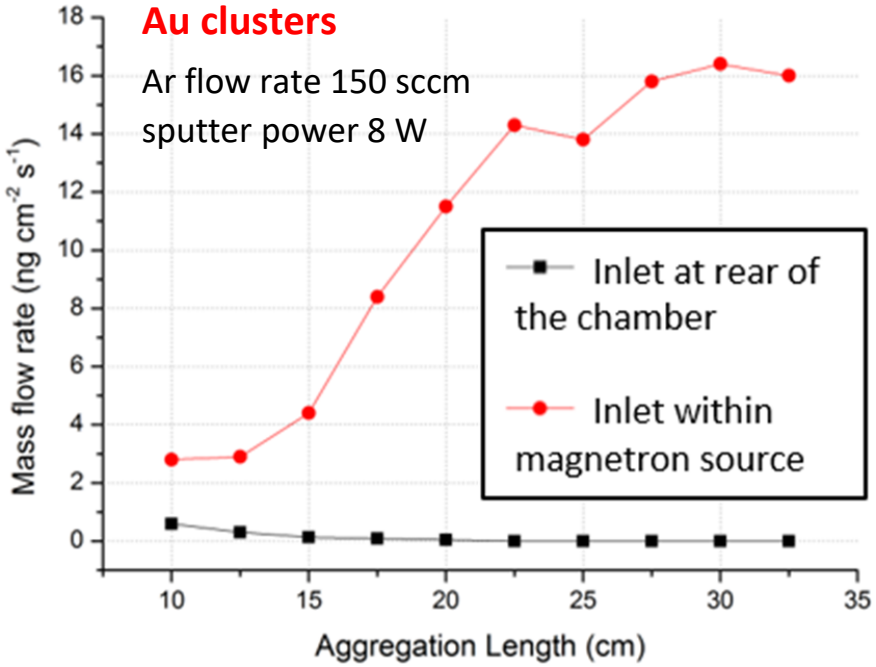


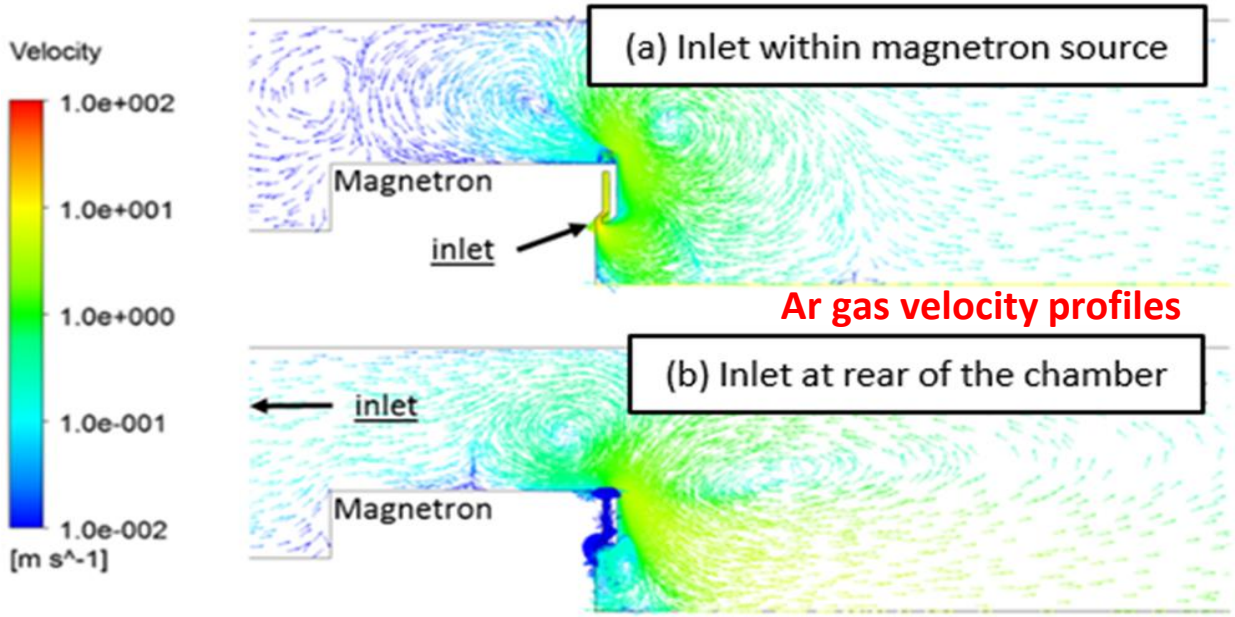


Parameters in a magnetron source

Gas inlet position







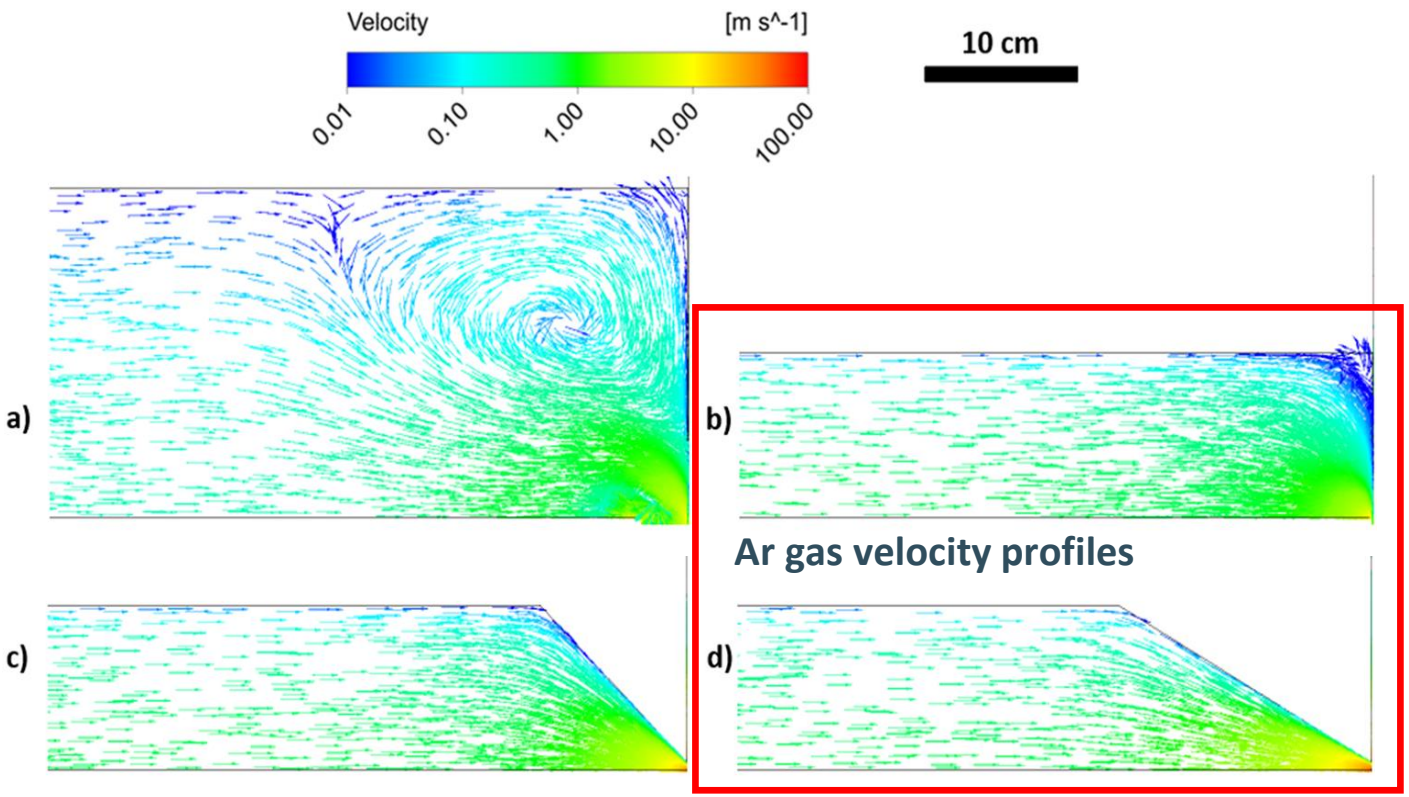
Cluster flux much higher if gas inlet is in magnetron.

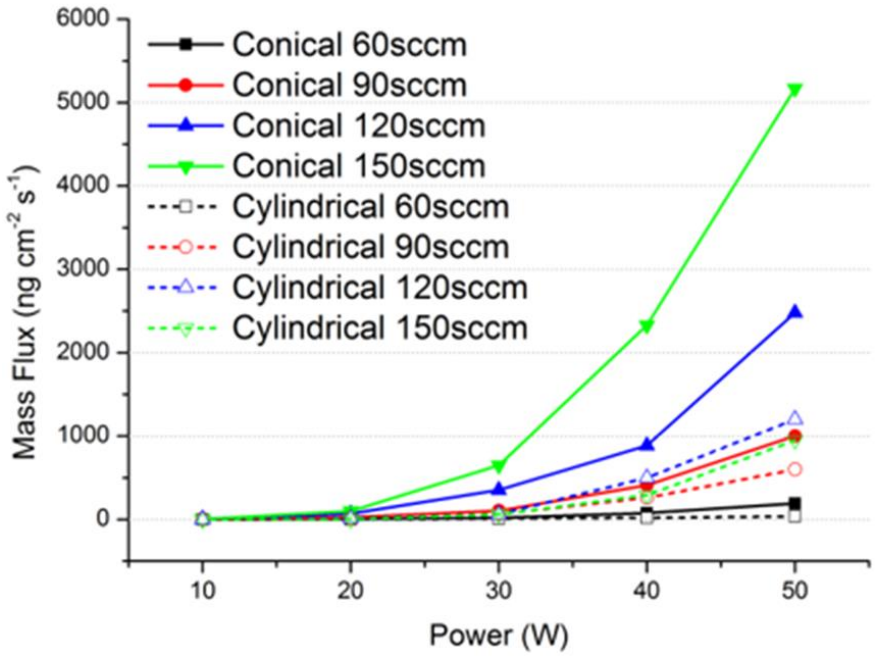
1) if inlet is at rear no large clusters are formed and small ones are more influenced by **Brownian motion** (get lost)
2) Ar velocity profile above target. **Drag force** stronger if gas inlet above target (less redeposition).

G. Sanzone, J. Yin, K. Cooke, H. Sun, P. Lievens, *Impact of the gas dynamics on the cluster flux in a magnetron cluster-source…*, Rev. Sci. Instrum. **92**, 033901 (2021)

Parameters in a magnetron source

Shape of the condensation chamber





Conical shaped aggregation chamber:
gas velocity close to the walls is higher
→ less attachment of clusters to walls.

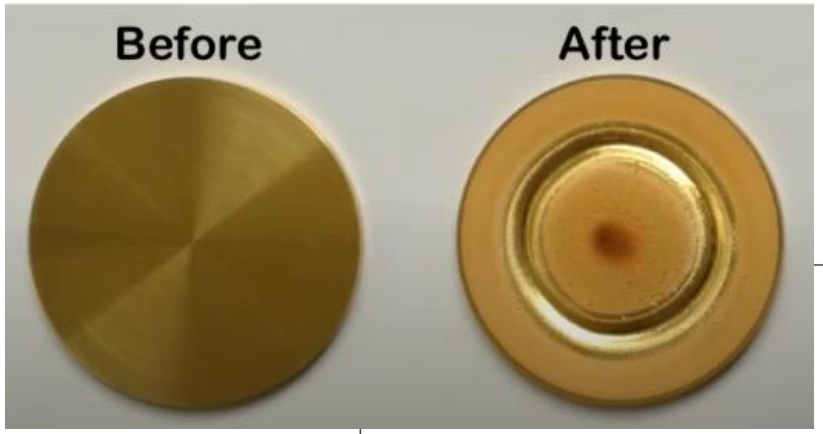
Aerodynamics in source is **important** for the cluster production.

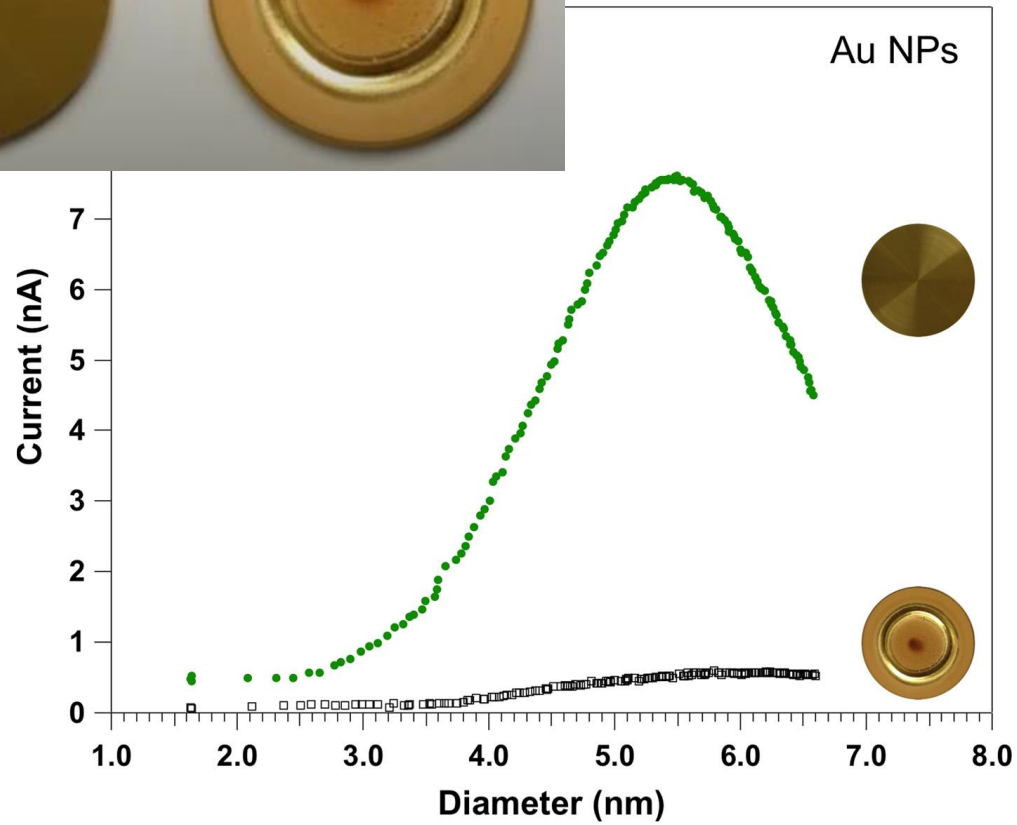
G. Sanzone, J. Yin, K. Cooke, H. Sun, P. Lievens, *Impact of the gas dynamics on the cluster flux in a magnetron cluster-source…*, Rev. Sci. Instrum. **92**, 033901 (2021)

Parameters in a magnetron source

Magnetic field

- Magnet array in magnetron sputtering extends path of electrons to anode, enhancing the chance they can ionize Ar and thereby also the sputtering yield.
- But formation of race track is source of instability → NP formation decreases in time and only small portion of target can be used (about 5%).





Y. Huttel, L. Martínez, A. Mayoral, I. Fernández, *Gas-phase synthesis of nanoparticles: present status and perspectives* , MRS Communications **8**, 947 (2018)

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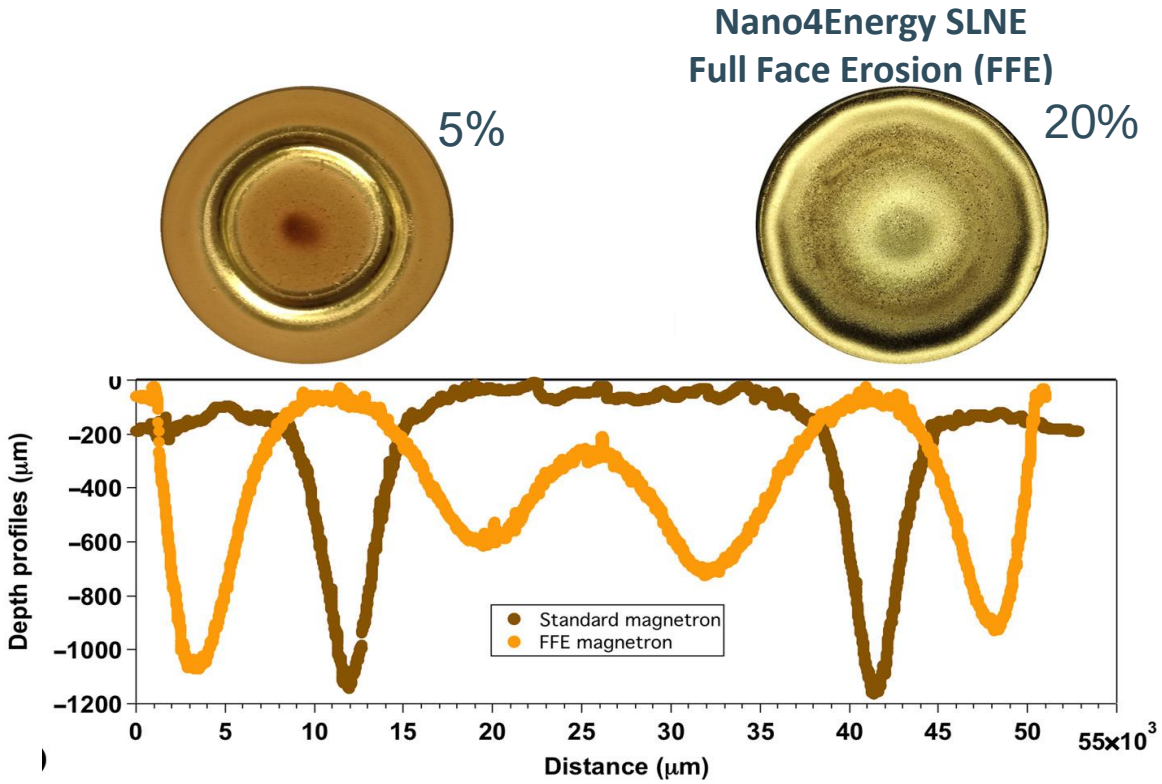
Magnetic field

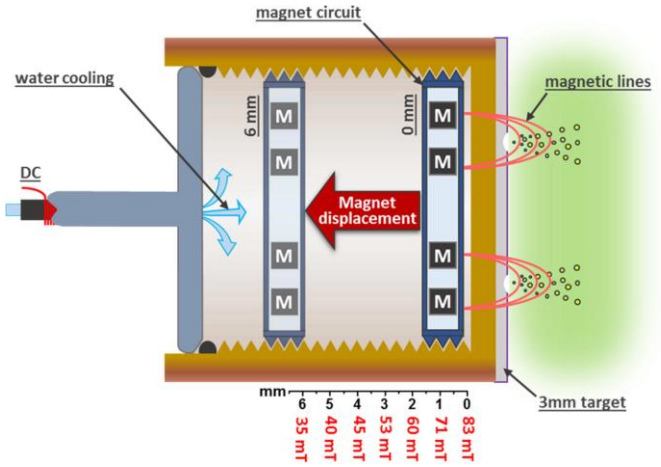
- Magnet array in magnetron sputtering extends path of electrons to anode, enhancing the chance they can ionize Ar and thereby also the sputtering yield.
- But formation of race track is source of instability → NP formation decreases in time and only small portion of target can be used (about 5%).
- Solution: move magnets to use entire target surface.

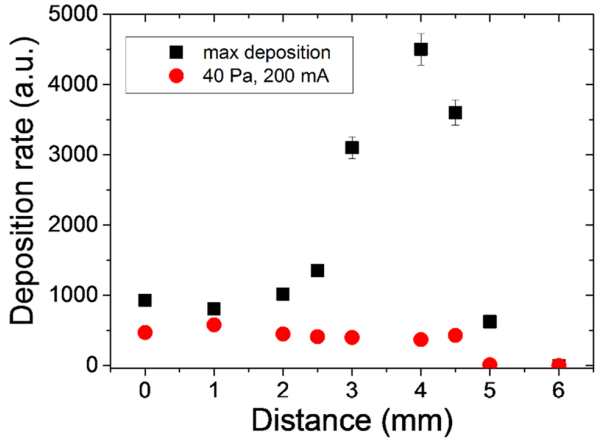


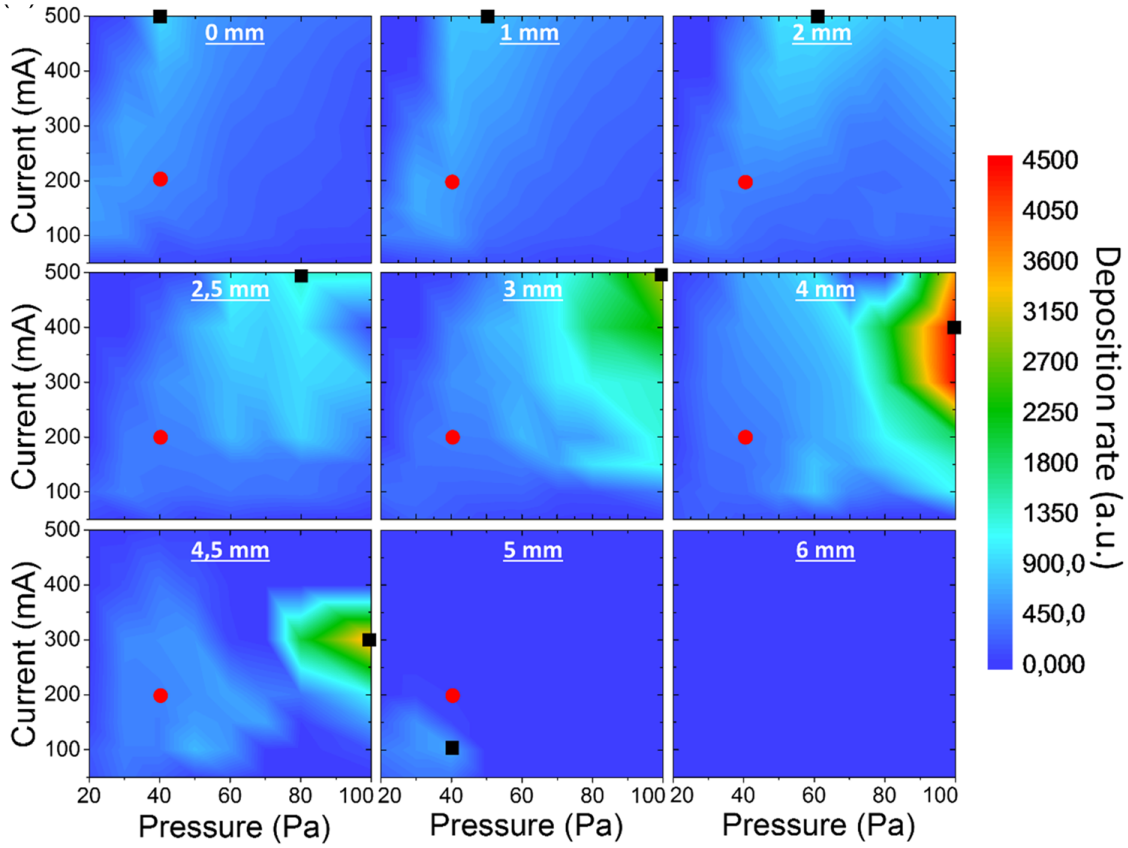
Y. Huttel, L. Martínez, A. Mayoral, I. Fernández, *Gas-phase synthesis of nanoparticles: present status and perspectives* , MRS Communications **8**, 947 (2018)

Parameters in a magnetron source

Magnetic field and electromagnetic trapping





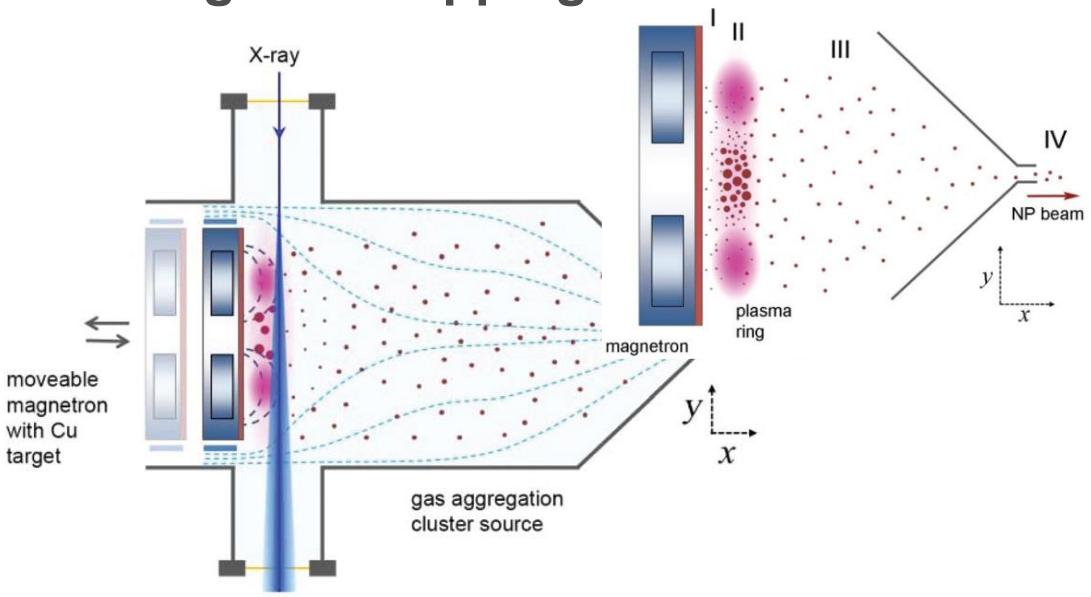


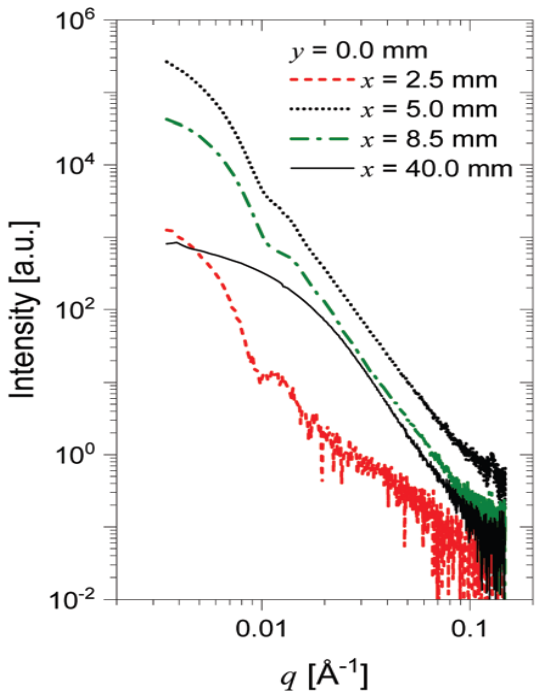
- Change of magnetic field (MF) strength: higher MF implies larger particles but also more trapping / difficult for particles to leave source and more redeposition on sputter target.
- With pressure increase, drag force is stronger and trapping efficiency weakens.

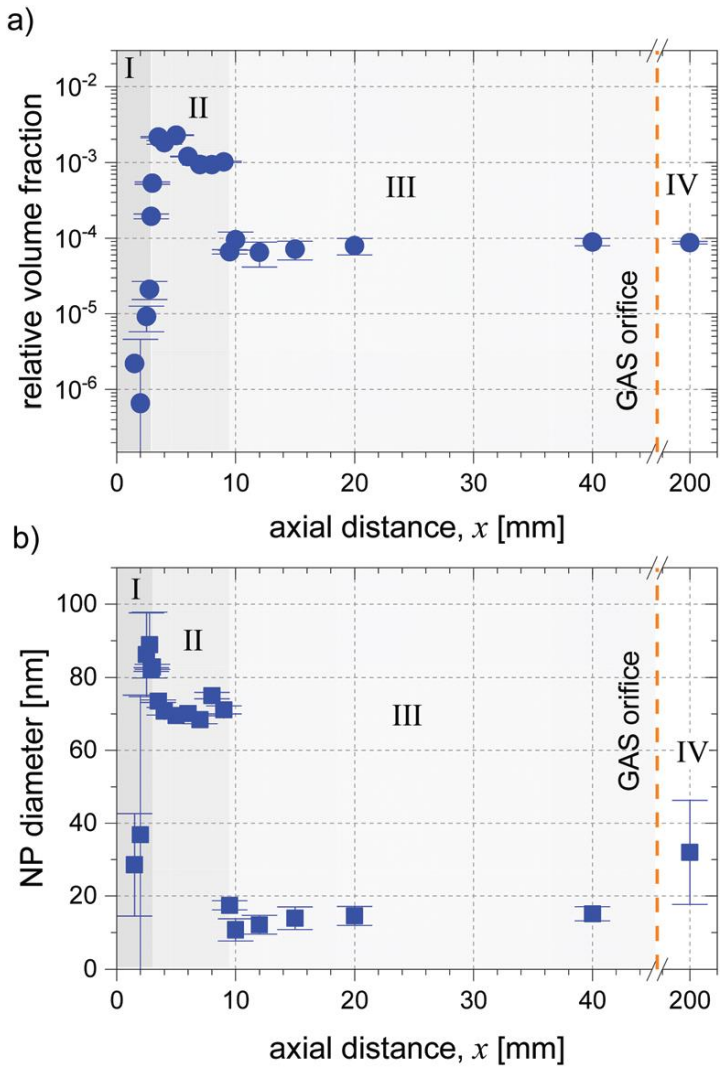
M. Vaidulych et al., Plasma Process Polym. e1900133 (2019)

Parameters in a magnetron source

Electromagnetic trapping





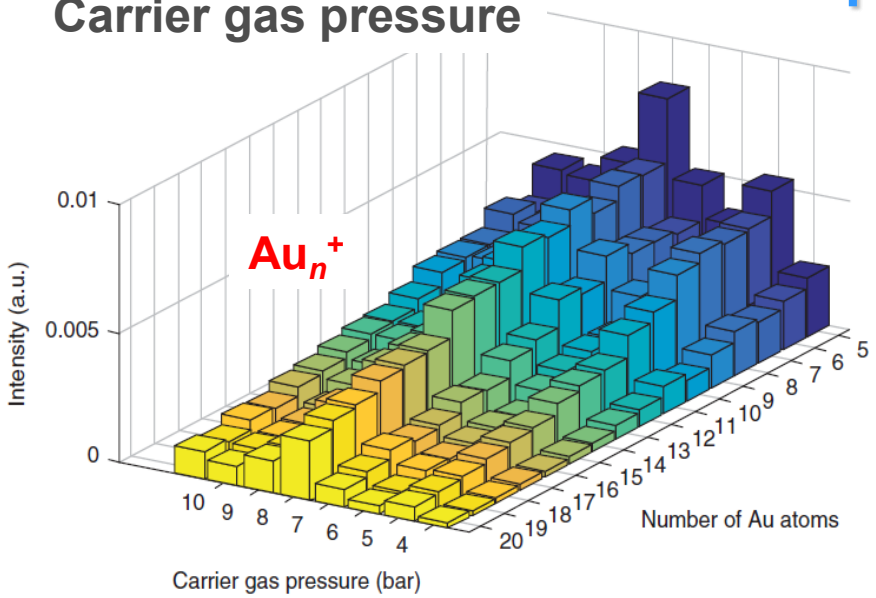


- Detailed understanding of growth kinetics still lacking
- X-ray scattering to probe position-dependent NP size distribution.
- Zone II (slightly above target) = **capture zone** contains very large **trapped particles** that don't get out of the source

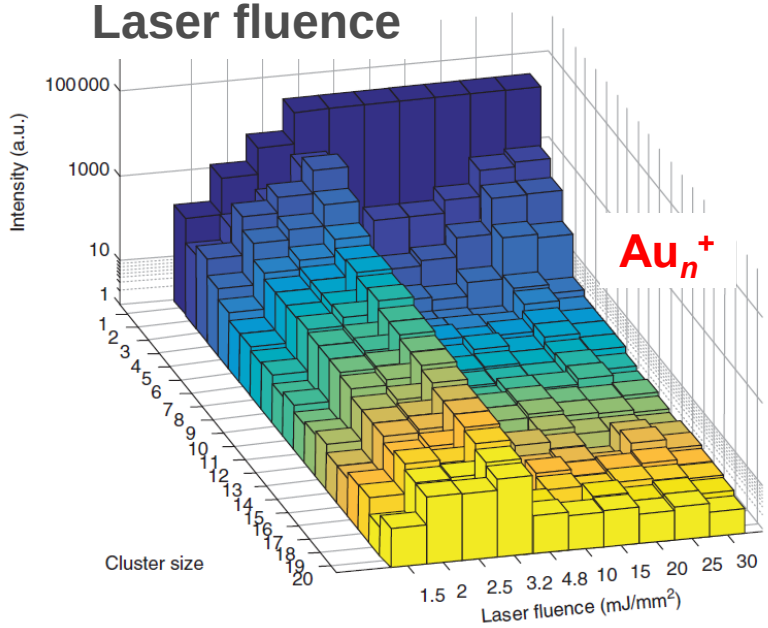
J. Kousal et al, Nanoscale **10**, 18275 (2018)

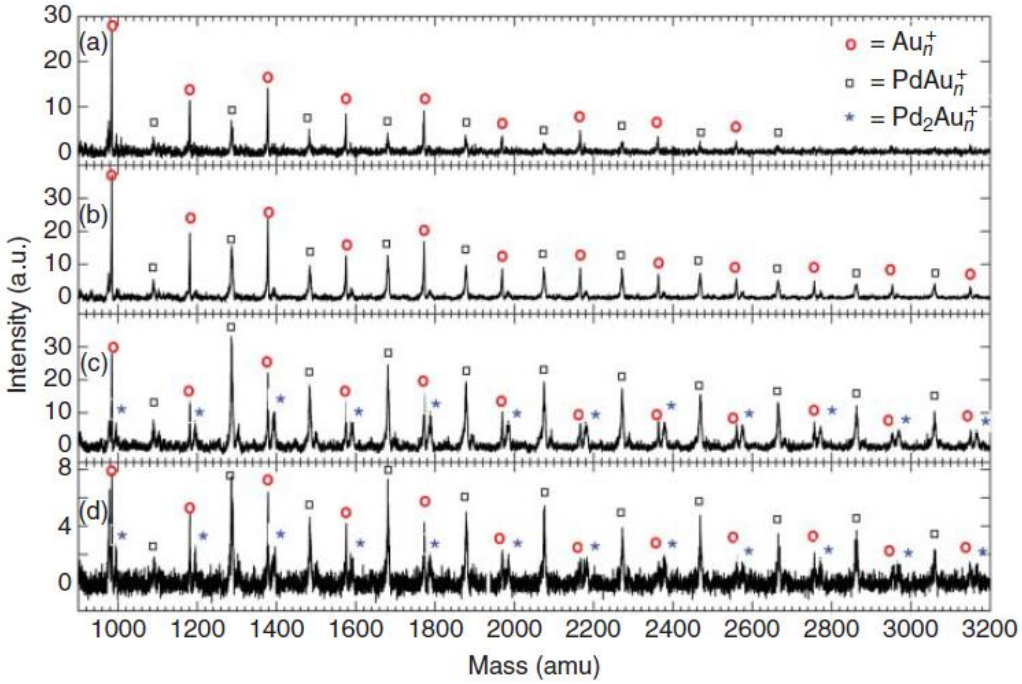
Parameters in pulsed laser ablation source

Carrier gas pressure



Laser fluence

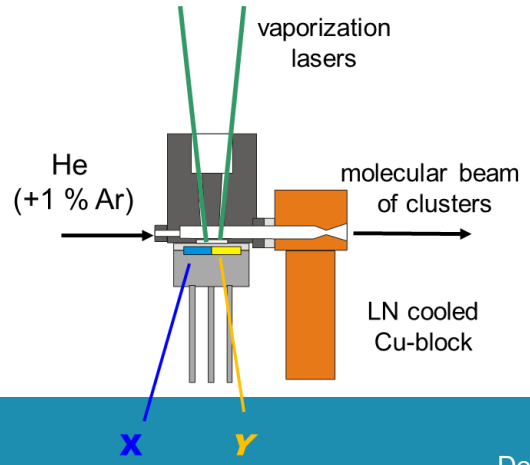




Au$_n$Pd$_{0-2}^+$

Laser fluence II

(a) Pure Au,
(b) E_{Pd} = 0.4 mJ/mm^2,
(c) E_{Pd} = 1.2 mJ/mm^2,
(d) E_{Pd} = 3.5 mJ/mm^2.



P. Ferrari, J. Vanbuel, T.W. Liao, E. Janssens, P. Lievens, *The double-laser ablation source approach* in *Gas aggregation synthesis of nanoparticles,* editor Y. Huttel, Wiley (2017)

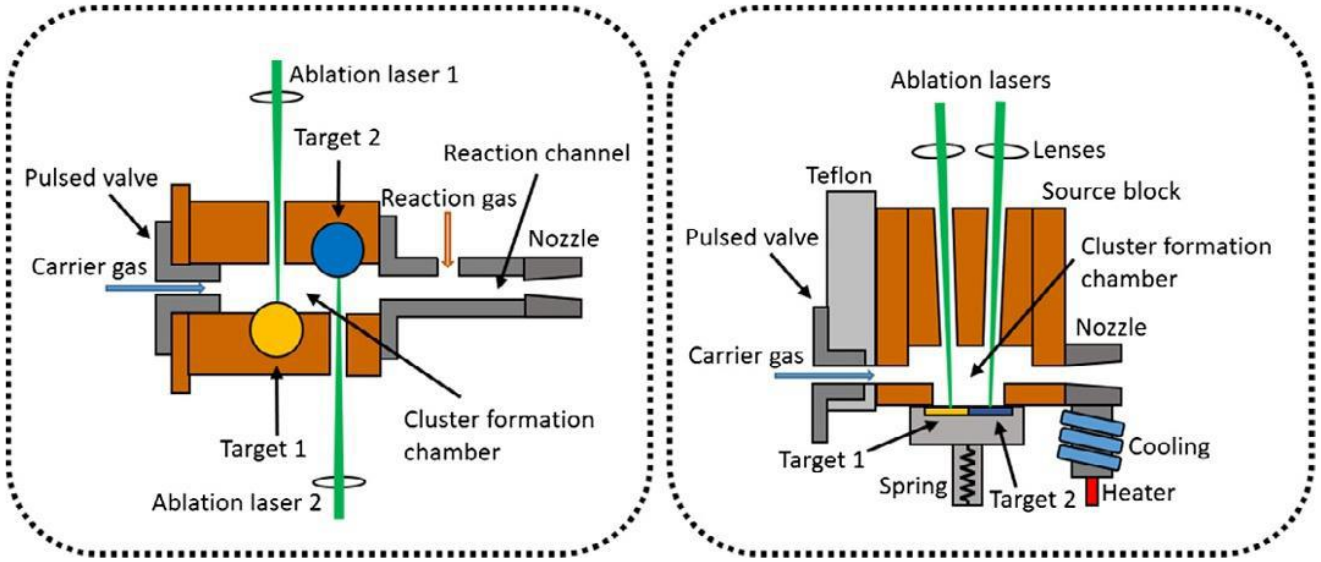
Outline Lecture

1) **General principles** of nanoparticle formation by gas phase aggregation
2) Influence of **source parameters** on the nanoparticle formation process
3) Growth of **nano-alloys** and out-of-equilibrium morphologies
4) **Scaling up** the production
5) **After production:** ion guiding, deposition, temperature in a cluster beam

Dual-target laser ablation source

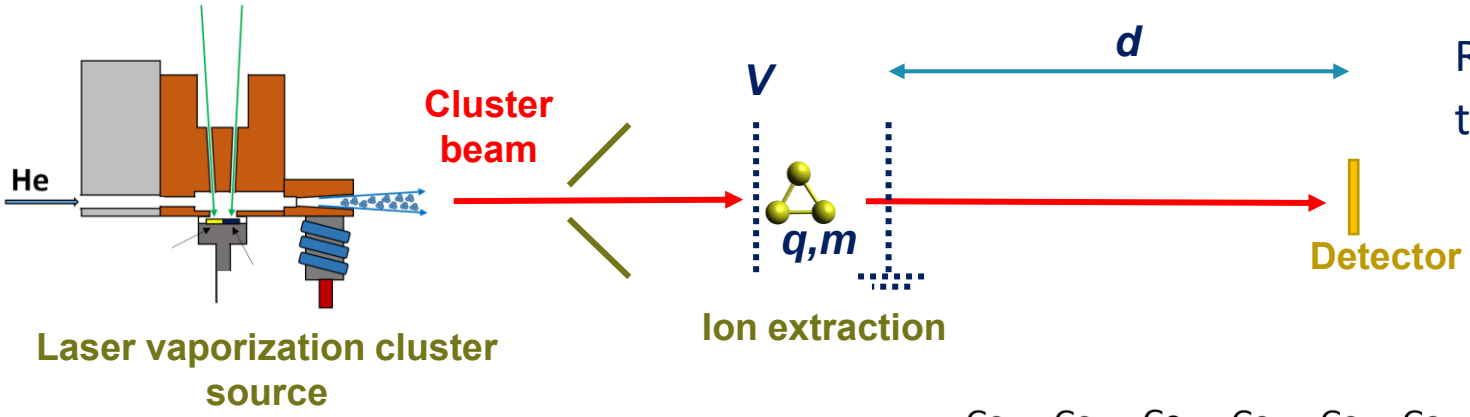
Characteristics

- Virtually any (solid) material can be used
- Fill source with (pulse of about 100 μs) carrier gas before laser ablation
- Targets constantly moved to ensure a fresh surface at every laser shot
- Tuning of size and composition via (independent) laser energy density, time delay between gas insertion and laser firing, gas pressure, source geometry (in particular nozzle diameter and shape)
- To study cluster reactivity, reactant gases can be inserted in reaction channel (after cluster formation)



Source figure: P. Ferrari, G. Sanzone, J. Yin, E. Janssens, *Physical synthesis of nanoalloys* in *Nanoalloys: from fundamentals to emergent applications,* editor F. Calvo, Elsevier (2020)

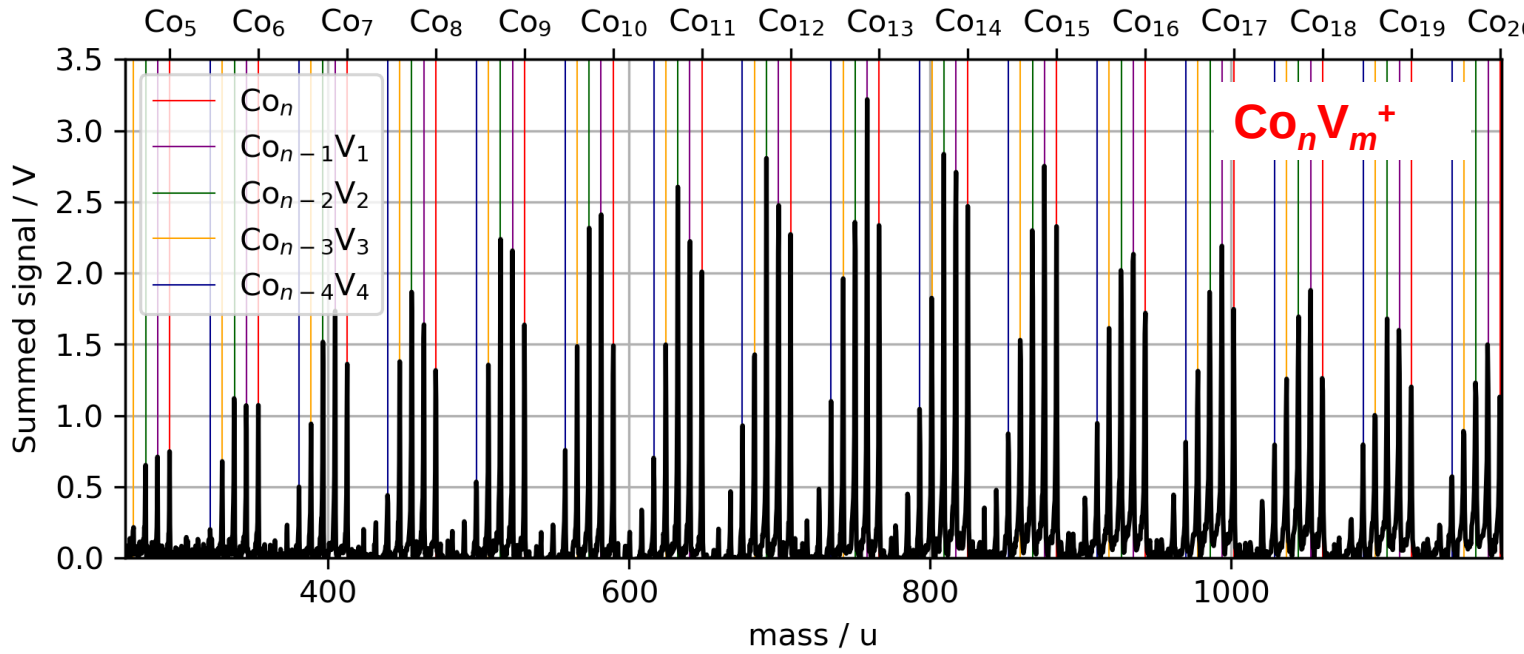
Time-of-flight mass spectrometry



Record flight times t of clusters (with charge q) that are accelerated by potential V

$$m = \frac{2qV}{d^2} t^2$$

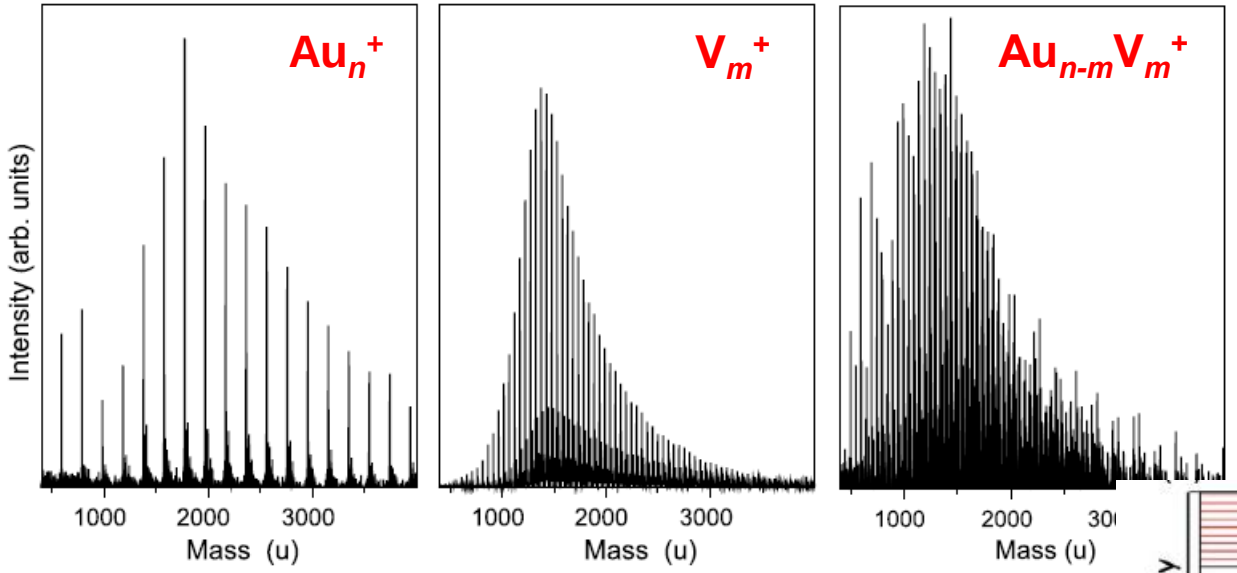
Example CoV mass spectrum



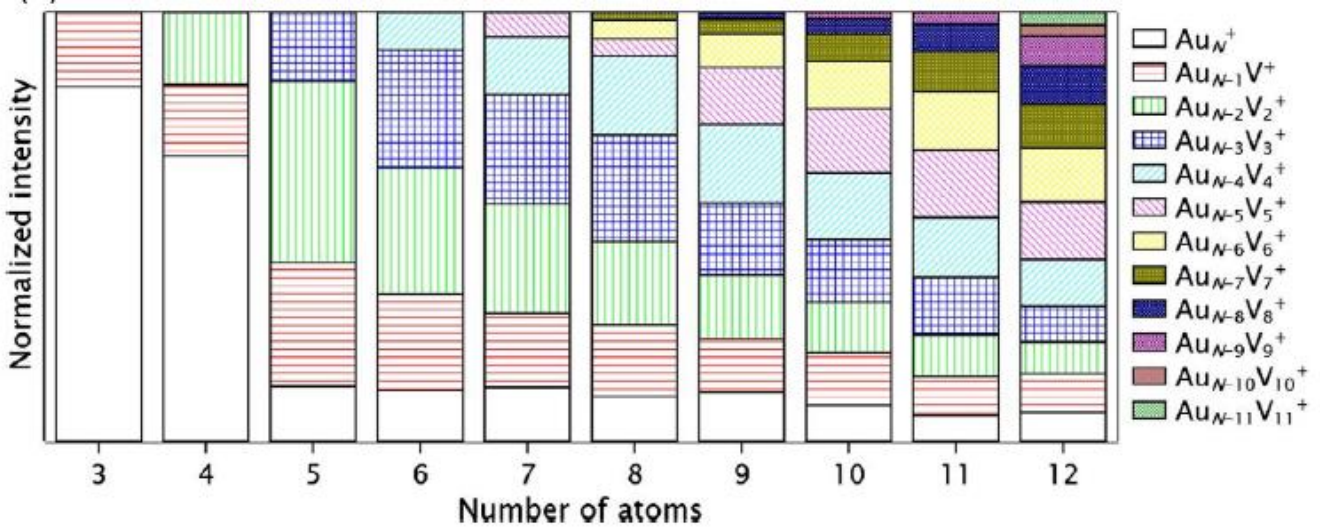
m_{Co} = 58.9 u, m_V = 50.9 u

Dual-target laser ablation source

Example



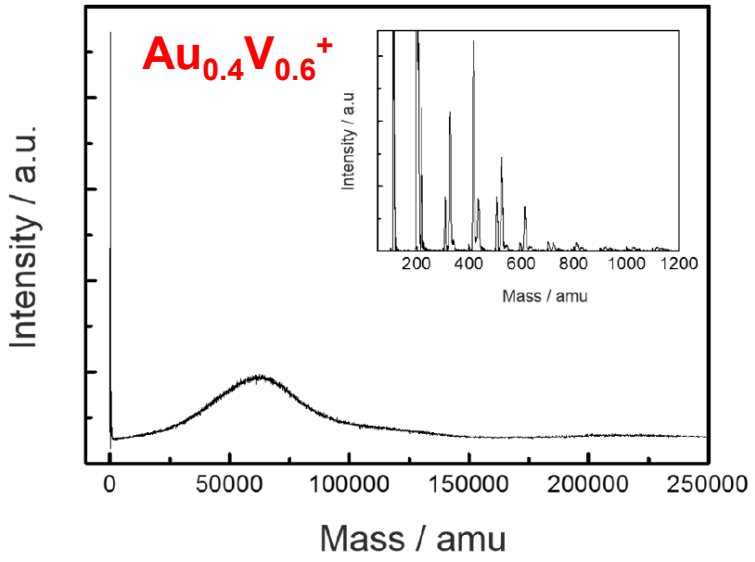
- Time-of-flight mass spectrometry used to measure size distribution.
- "Control" over average size and composition, but one always gets a distribution.

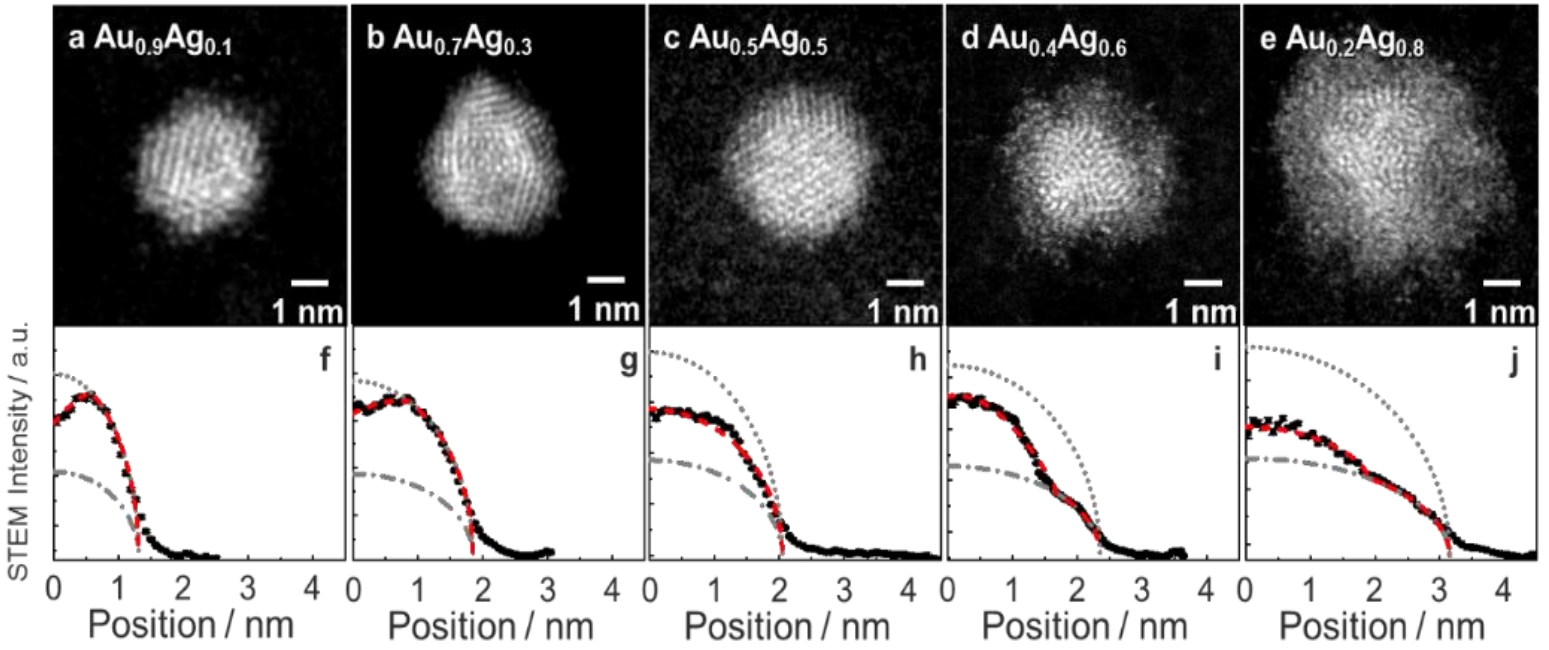


Source figure: P. Ferrari, G. Sanzone, J. Yin, E. Janssens, *Physical synthesis of nanoalloys* in *Nanoalloys: from fundamentals to emergent applications,* editor F. Calvo, Elsevier (2020)

Laser ablation of alloy targets

AuAg alloys with different compositions





- Clusters made (about 3 nm) of Au_xAg_{1-x} with x = 0.9, 0.7, 0.5, 0.4, 0.2 and deposited on TEM grids.
- For all compositions: core enriched in minority element, majority element forms shell. $Au_{0.5}Ag_{0.5}$ is an alloy.

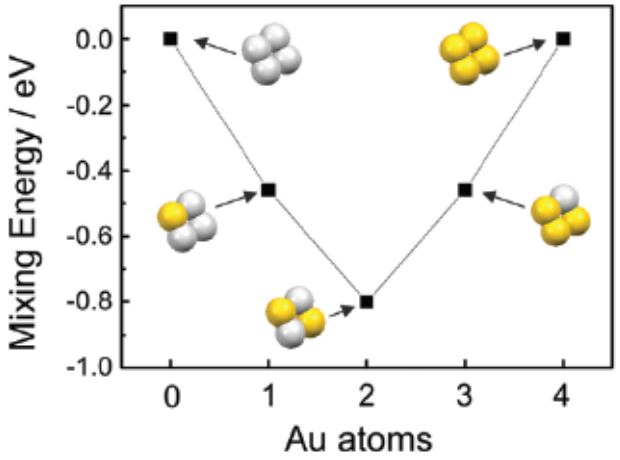
Radial intensity profiles: red dash lines are the simulations of cluster HAADF-STEM intensity with gradient composition evolution. Grey dotted lines and grey dash dotted lines are simulated intensities with pure Au clusters and pure Ag clusters.

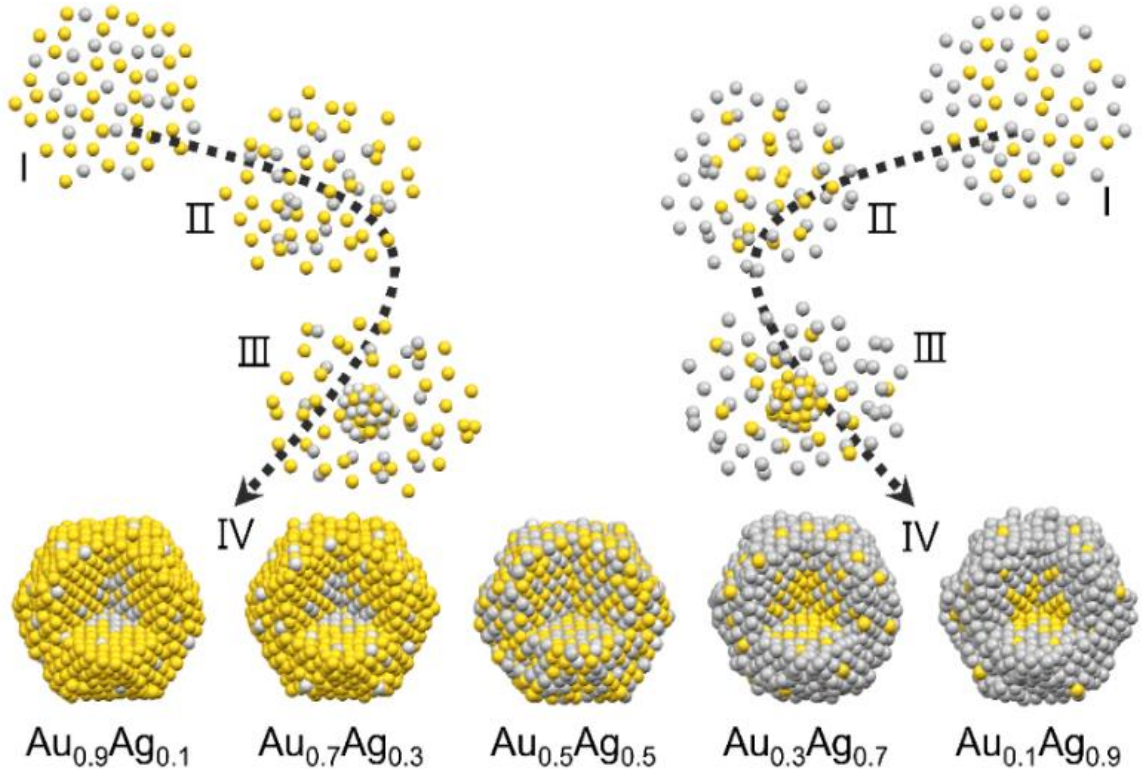
T.W. Liao, A. Yadav, K.J. Hu, J. van der Tol, S. Cosentino, F. D'Acapito, R.E. Palmer, C. Lenardi, R. Ferrando, D. Grandjean, P. Lievens. *Nanoscale* **10**, 6684 (2018).

Laser ablation of alloy targets

Formation mechanism

- Hetero Au-Ag stronger than homo Au-Au or Ag-Ag bonds so AuAg is most likely nucleation center.
- Serves as seeds for the growth of larger clusters, which form the nanoparticle core
- The remaining atoms of the majority element aggregate onto the preformed bimetallic core.
- A similar core–shell structural arrangement observed in bimetallic Ni–Pt clusters.



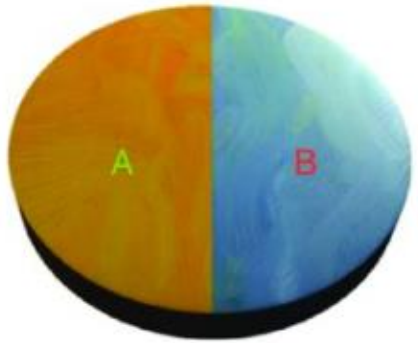


T.W. Liao, A. Yadav, K.J. Hu, J. van der Tol, S. Cosentino, F. D'Acapito, R.E. Palmer, C. Lenardi, R. Ferrando, D. Grandjean, P. Lievens. *Nanoscale* **10**, 6684 (2018).

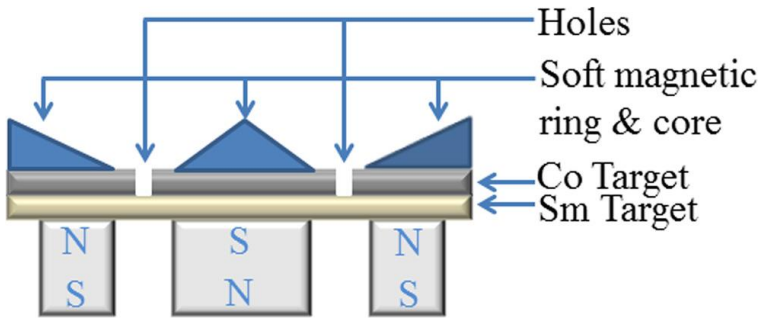
Nanoalloys in a magnetron source

Different strategies

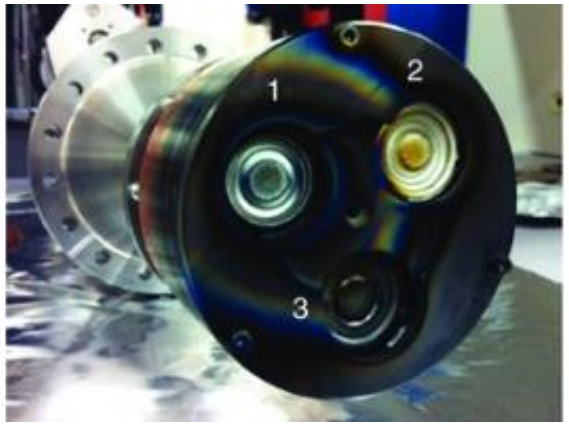
- Alloy sputter targets
  (only for miscible materials and stoichiometry limited to available alloys)
- Use of sectioned targets
  (no independent sputter power)
- In-plane multimagnetron
- Adjustable multimagnetron
- ….



G. Krishnan, M.A. Verheijen, G.H. ten Brink, G. Palasantzas, B.J. Kooi, Nanoscale **5**, 5375 (2013)



S.H. He, Y. Jing, J.P. Wang, J. Appl. Phys. **113**, 134310 (2013)



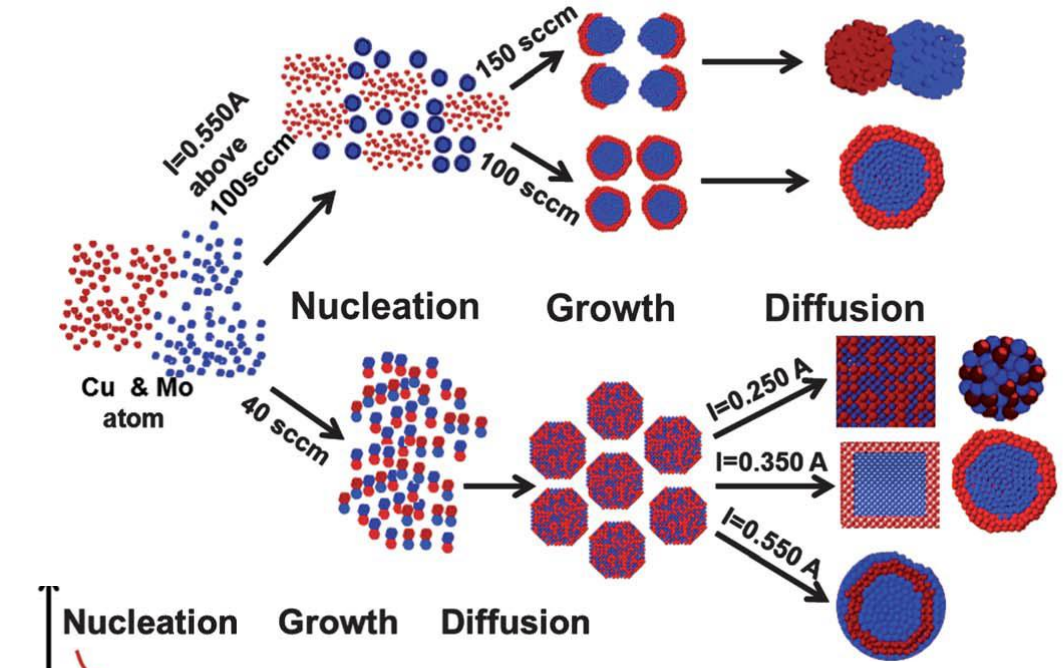
V. Singh, C. Cassidi, P. Grammatikopoulos, F. Djurabekova, K. Nordlund, M. Sowwan, J. Phys. Chem. C. **118**, 13869 (2014)

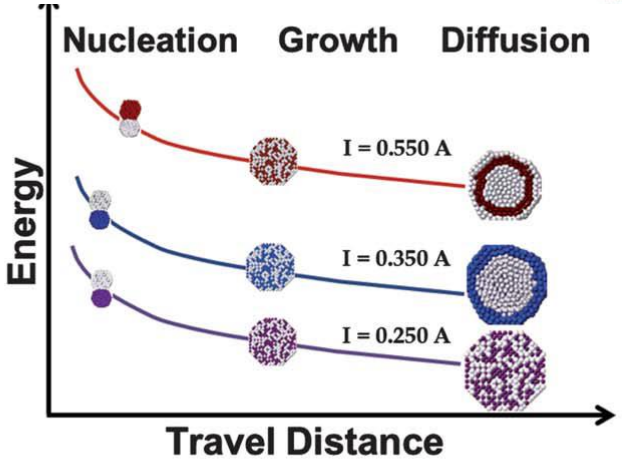
D.L. Perez, L. Martinez, Y. Huttel, Dataset Paper in Science, 584391 (2014)

Nanoalloys in a magnetron source

Single magnetron with sectioned target

- Sectioned target ½ Mo - ½ Cu (Mo and Cu immiscible in bulk)
- Thermal environment tuned by **discharge current** and **Ar flow rate**. Particles deposited on SiN membrane and characterized by TEM
- Distinctively different CuMo NP morphologies obtained → trapping in **non-equilibrium structures**
- With low gas flow rate, cooling is slow and reconstruction to cube (the preferred NP shape of pure Mo) can occur (not for high gas flow rate) at the relatively low discharge current (0.250 A). In this case energy gained by Cu atoms in the plasma is sufficient for mixing and formation of Mo–Cu solid solution, but not to overcome the energy barrier for phase separation and Mo–Cu core–shell formation



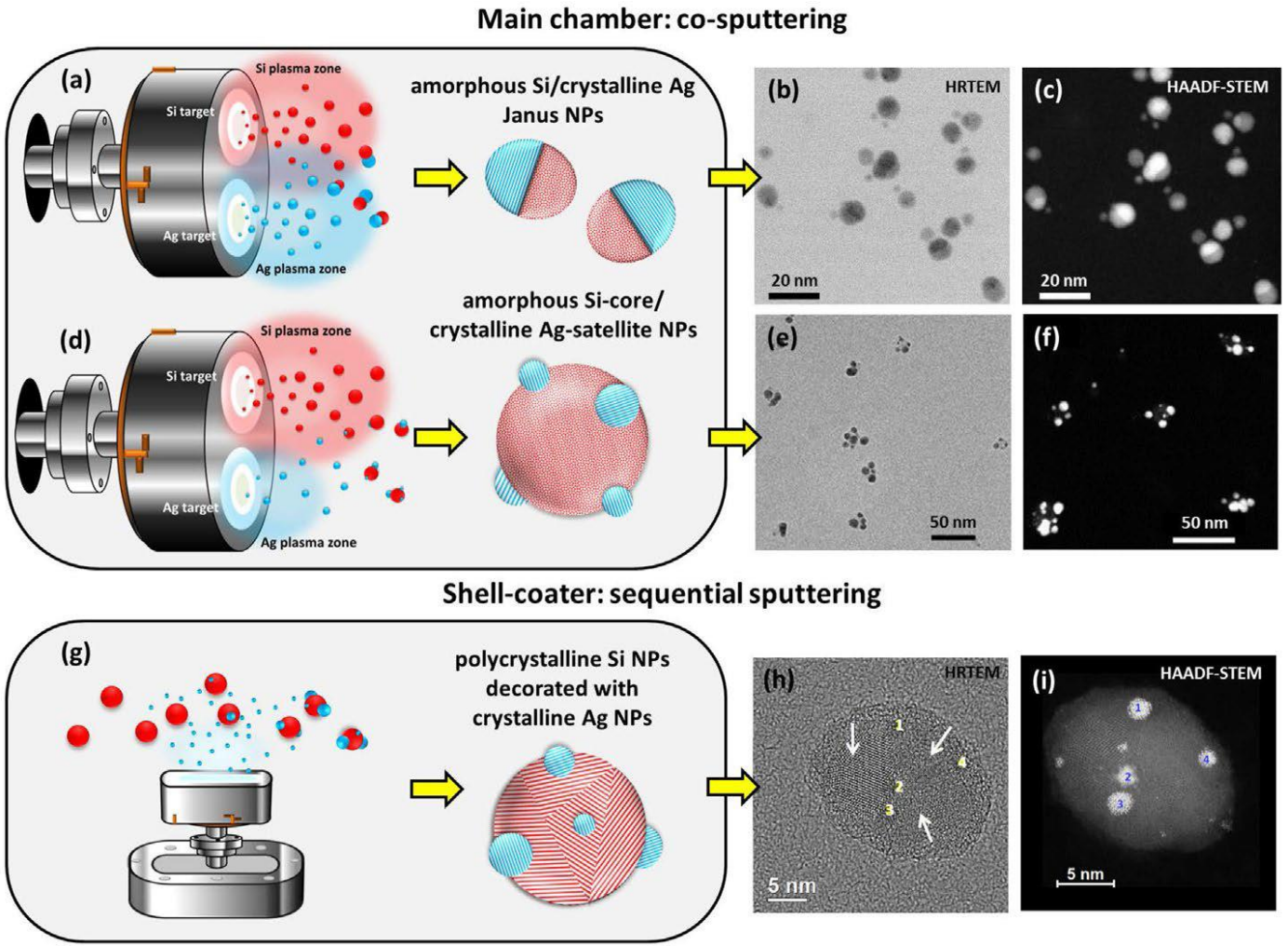


G. Krishnan, M.A. Verheijen, G.H. ten Brink, G. Palasantzas, B.J. Kooi, *Tuning structural motifs and alloying of bulk immiscible Mo–Cu bimetallic nanoparticles by gas-phase synthesis,* Nanoscale **5**, 5375 (2013)

Nanoalloys in a magnetron source

In-plane multimagnetron

- (a-c) Si and Ag clusters grow separate and coalesce in aggregation zone → **Janus type NPs**
- (d-f) If density of Si is initially higher than that of Ag → **amorphous Si core with crystalline Ag satellites**
- (g-i) Ag atoms condense on (**polycrystalline**) Si NP **after NPs left** the **aggregation zone** → **Si core with Ag satellites**. Ag evaporated by separate magnetron in a **shell coater**.

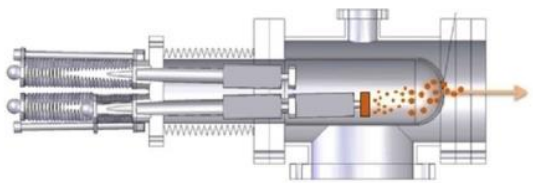


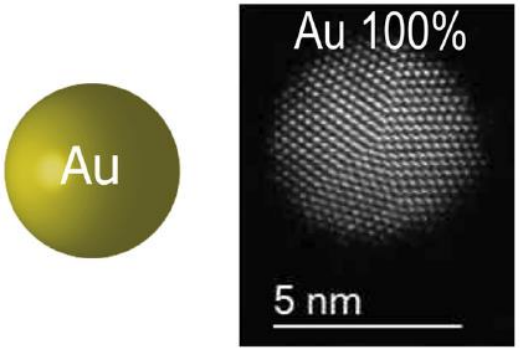
P. Grammatikopoulos, S. Steinhauer, J. Vernieres, V. Singh, M. Sowwan *Nanoparticle design by gas-phase synthesis*, Adv. Phys. X, **1**, 81 (2016).

Nanoalloys in a magnetron source

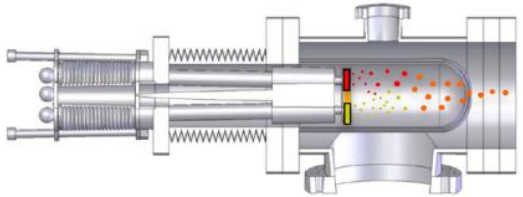
Adjustable multimagnetron (MICS)

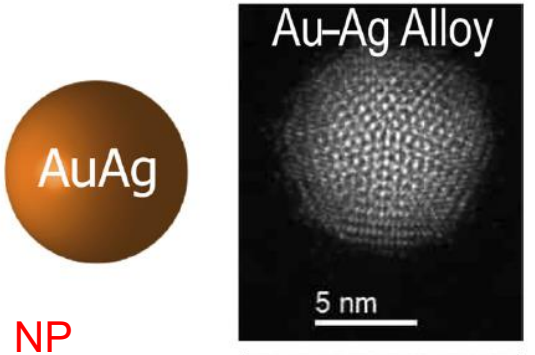
- Multiple **independent magnetrons** (invented in 2010 by ICMM-CSIC; licensed to Oxford Applied Research).
- **MICS** (multiple ion cluster source), provides a **high flexibility** on NP morphologies.
- Growth relies on sticking coefficients, not on chemical reactions → allows fabrication of **NPs not accessible by chemical methods**.



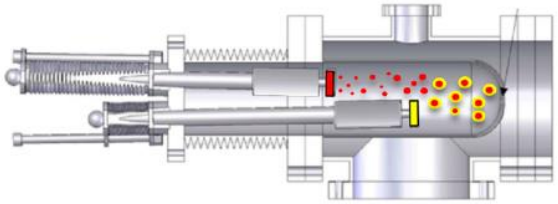


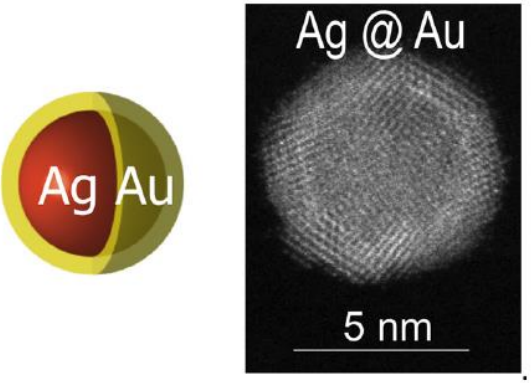
Single element NP





Homogeneously alloyed NP





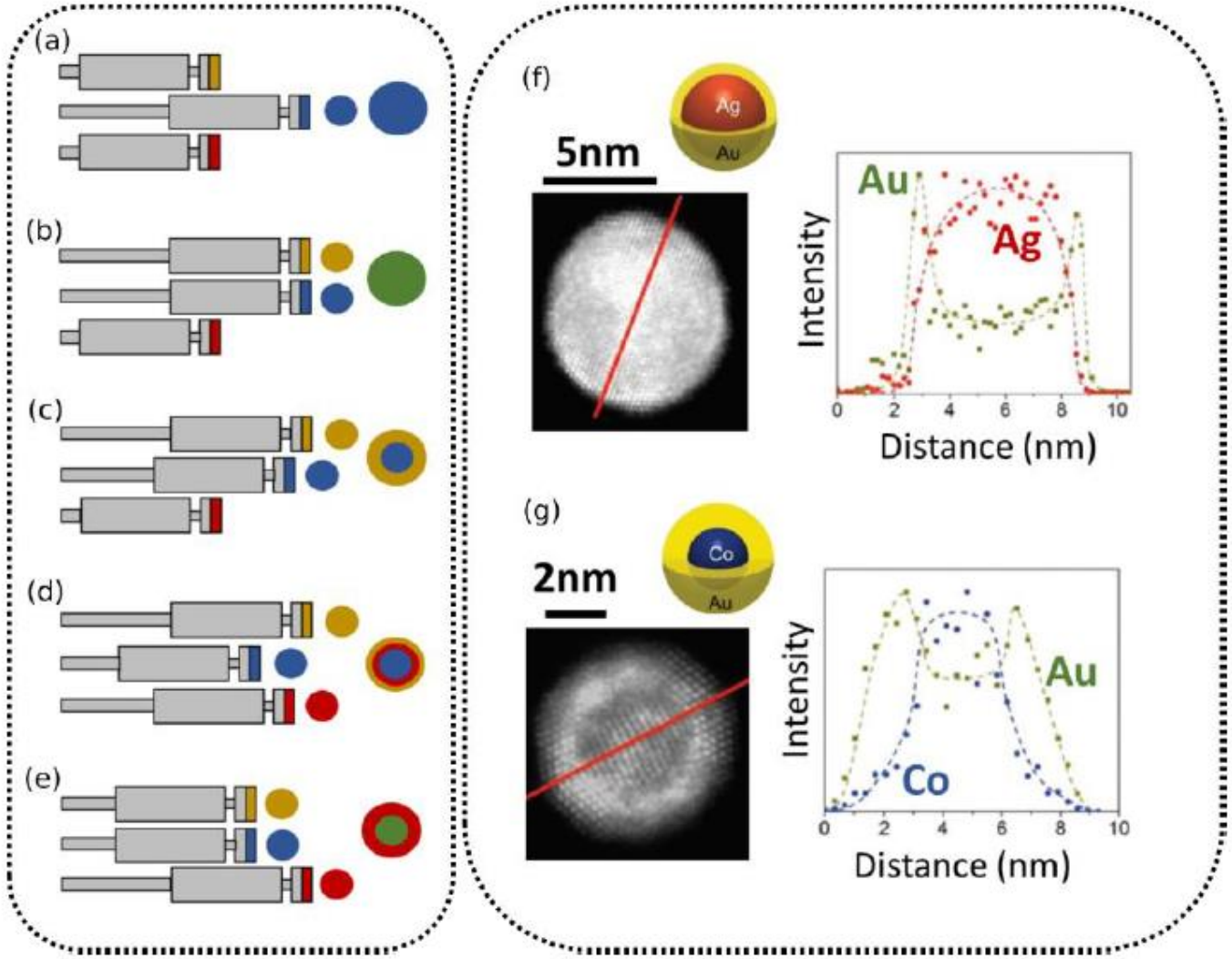
Core-shell NP

Y. Huttel, L. Martínez, A. Mayoral, I. Fernández, *Gas-phase synthesis of nanoparticles: present status and perspectives* , MRS Communications **8**, 947 (2018)

Nanoalloys in a magnetron source

(a) to (e) Illustration of possible configurations in a nanocluster magnetron source with three independent sputter heads (different materials) and the resulting possible different atomic arrangements of the produced NPs.

(f) and (g) TEM images and EDS line scans of two particles using the source configurations presented in (c).



D. Llamosa, M. Ruano, L. Martínez, A. Mayoral, E. Roman, M. García-Hernández, Y. Huttel, *The ultimate stop towards a tailored engineering of core@shell and core@shell@shell nanoparticles*, Nanoscale **6**, 13483 (2014)

Outline Lecture

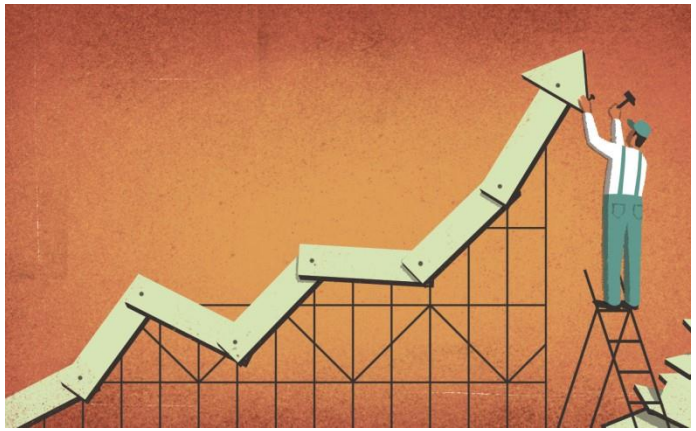
1) **General principles** of nanoparticle formation by gas phase aggregation
2) Influence of **source parameters** on the nanoparticle formation process
3) Growth of **nano-alloys** and out-of-equilibrium morphologies
4) **Scaling up** the production
5) **After production:** ion guiding, deposition, temperature in a cluster beam

Required amounts

Some numbers for catalysis, similar reflections can be made for optics, medical applications, magnetism….

- **Typical cluster sources** produce 100 pA – 1 nA (or 10^9 – 10^{10} s^{-1}) of size-selected charged clusters. For Pd_{200}^+ this corresponds to **0.1 – 1.0 µg/h**. This is enough for surface science research / sensitive characterization techniques.

- "Traditional" **catalyst evaluation** requires a few 100 mg of catalyst containing about 1% NPs or **few mg NPs**, what would imply 1000 h of deposition is size-selection is requested.
- For **industrial applications** with a target production rate of 1– 10 kg catalyst per day or **10-100 g NPs** (1% loading) another factor 10^4-10^5 increase is required to reach 1 g/h or more.
- **Scale-up is needed**.

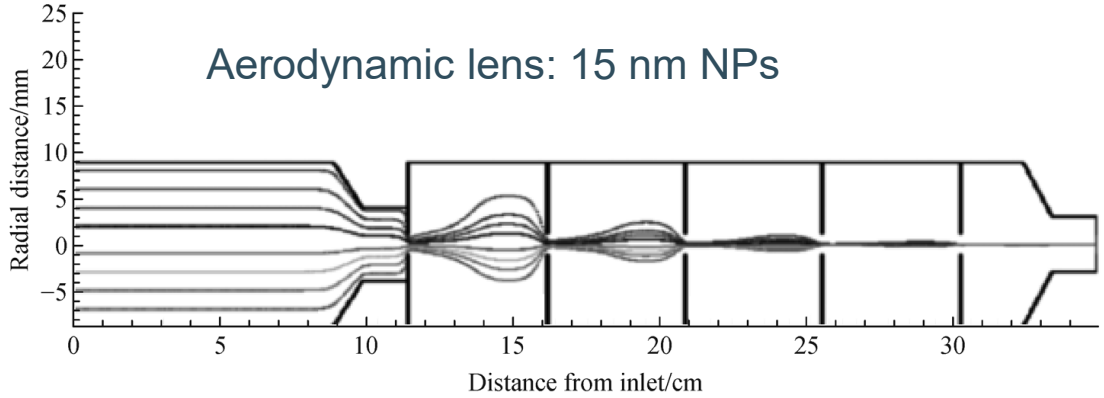


Good recent reference: G. Sanzone, J. Yin, H. Sun, *Scaling up of cluster beam deposition technology for catalysis application*, Front. Chem. Sci. Eng. **15**, 1360-1379 (2021)

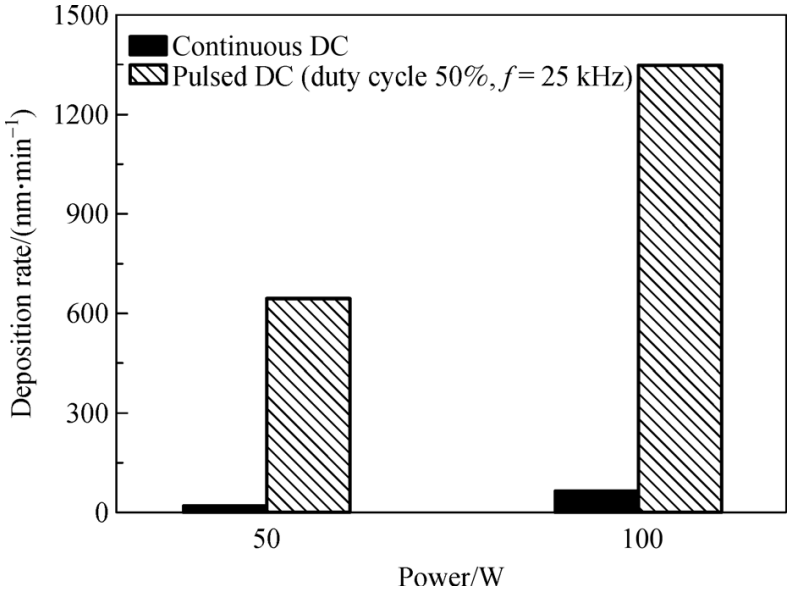
Strategies to increase yield

General

- No size selection, deposit entire size distribution
- Optimize the gas dynamics within the source (cf. earlier)
- Use aerodynamics lens after source



K. Wegner, P. Piseri, H.V. Tafreshi, P. Milar
J. Phys. D: Appl. Phys. **39**, R439 (2006)



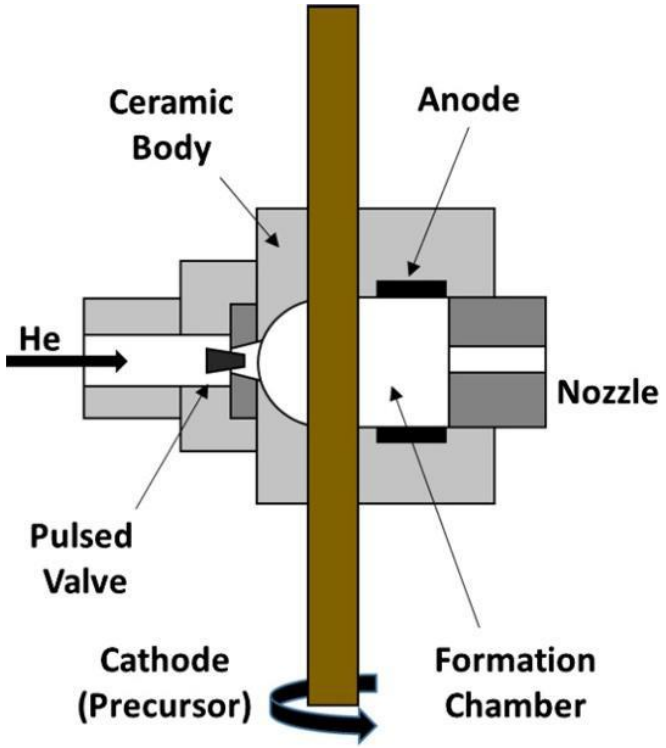
O. Polonskyi et al., Appl. Phys. Lett. **103**, 033118 (2013)

Scaling up the magnetron sputtering source

- Optimize magnetic field effects / particle trapping (cf. earlier)
- Use larger and multiple magnetrons (MICS)
- Increase power of discharge, while avoiding overheating, by high power impulse magnetron sputtering (HiPIMS)
- ….

Strategies to increase yield

Pulsed microplasma cluster source (PMCS)

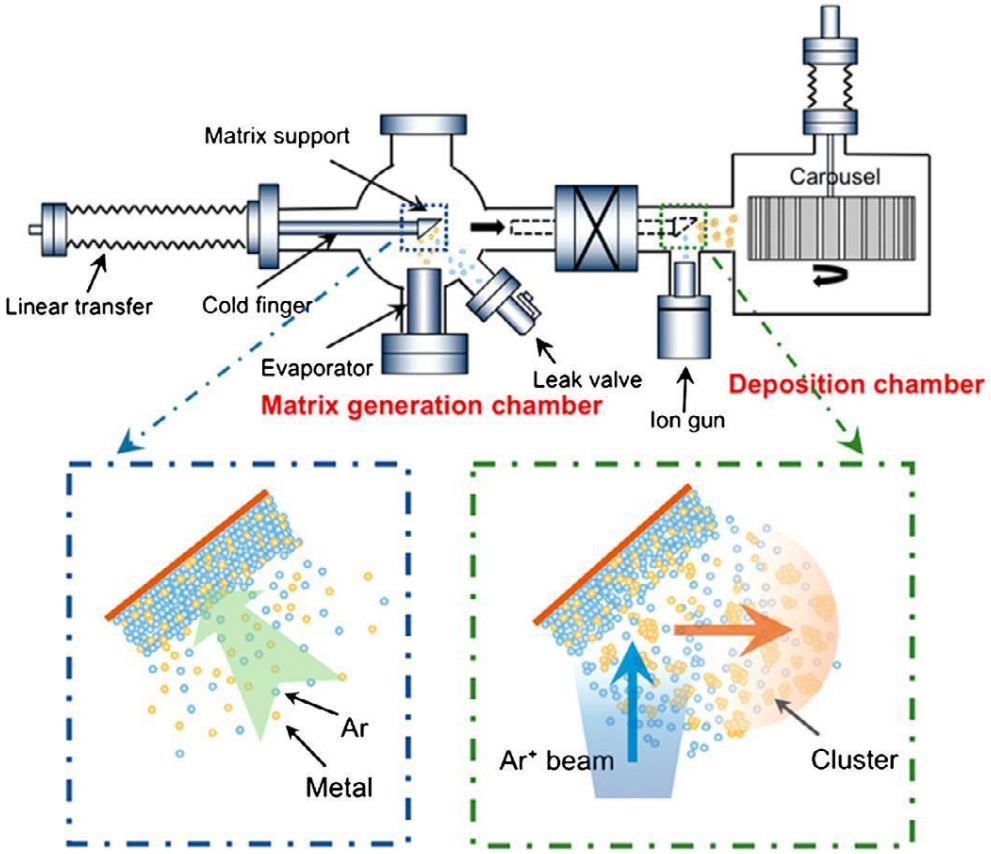


- Similar idea as the pulsed arc cluster ion source (PACIS)
- Space surrounding cathode and anode is larger and gap between cathode and anode does face pulsed gas valve.
- Localized plasma erosion on cathode
- May be equipped with aerodynamic lenses

E. Barborini, P. Piseri, P. Milani, *A pulsed microplasma source of high intensity supersonic carbon cluster beams,* J. Phys. D: Appl. Phys. **32** , L105-L109 (1999)

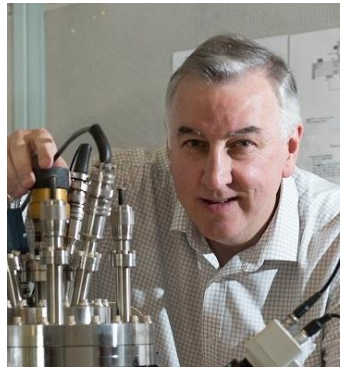
Strategies to increase yield

Matrix assembly cluster source (MACS)



- New operation principle (first reported in 2016)
- Step 1 – grow matrix: condense atomic vapor of material of interest in cold solid Ar matrix (~10 K)
- Step 2 – deplete matrix: energetic Ar^+ ions initiate collision cascade that leads to cluster growth and ejection of neutral particles.

More in Richard's talk this afternoon



R.E. Palmer, L. Cao, F. Yin F, Rev. Sci. Instrum. **87**, 046103R (2016)
R.E. Palmer, R. Cai, J. Vernieres, Acc. Chem. Res. **51**, 2296 (2018)

Outline Lecture

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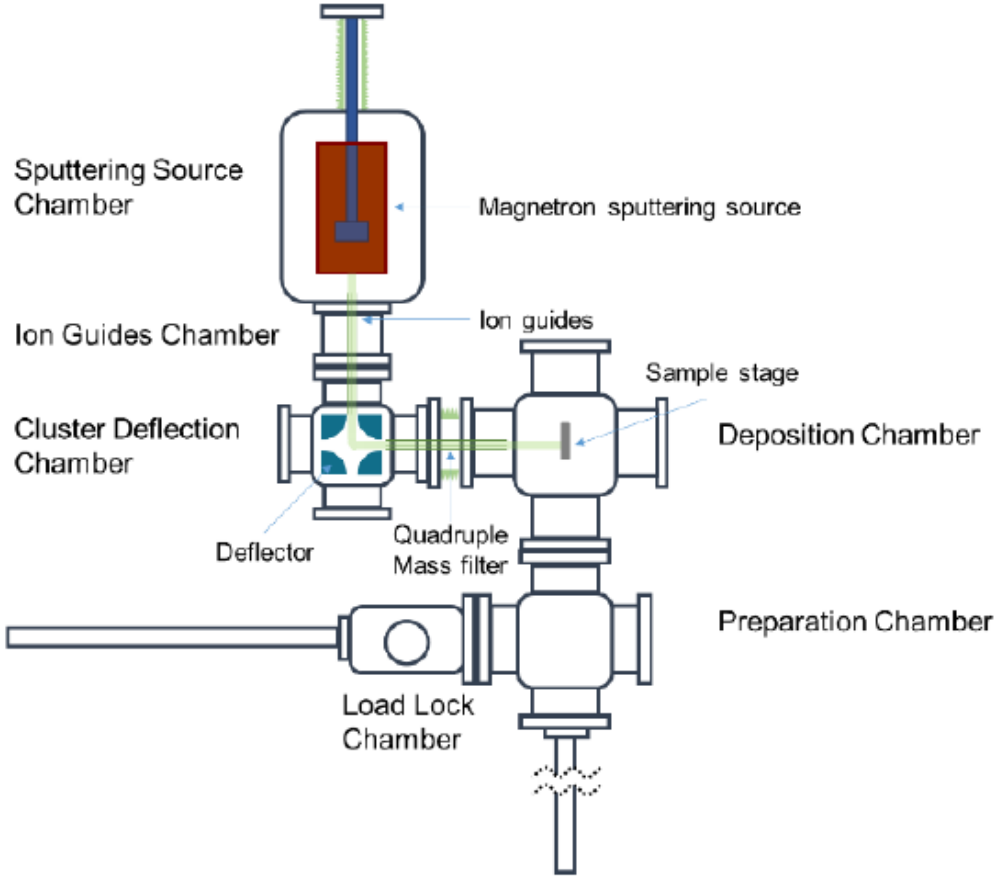
From source to substrate

Cluster beam deposition in vacuum

- Neutrals: no guiding possible, only aerodynamic lenses to focus beam and perform rough mass selection.
- Ions: ion guiding and mass filtering
  - Einzel lens, RF ion guide, quadrupole bender… (all to some extent mass dependent)
  - Quadrupole mass filter, time-of-flight mass filter…
  - Possibility to tune interaction by impact energy of particles (can be accelerated/decelerated)
- Possibility to co-evaporate a matrix material (nanoparticles/clusters in matrix) or deposit a protecting cover layer.

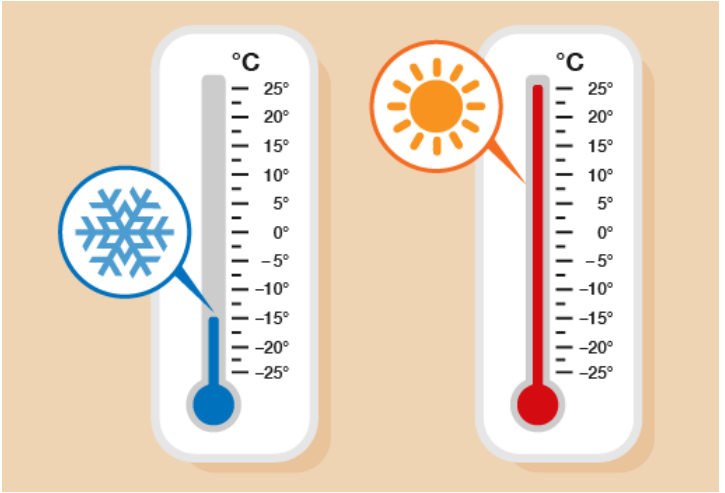
Fractions of charged clusters in different sources:
thermal source 0%, laser vaporization ~ 10%,
magnetron source up to 50%, PMCS 10%, MACS 0%



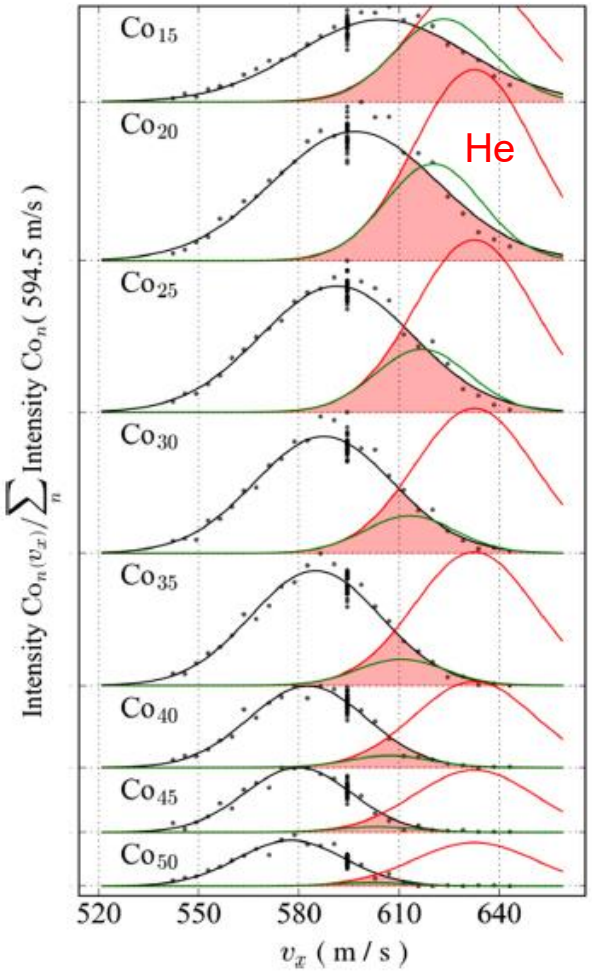
At last a comment on temperature

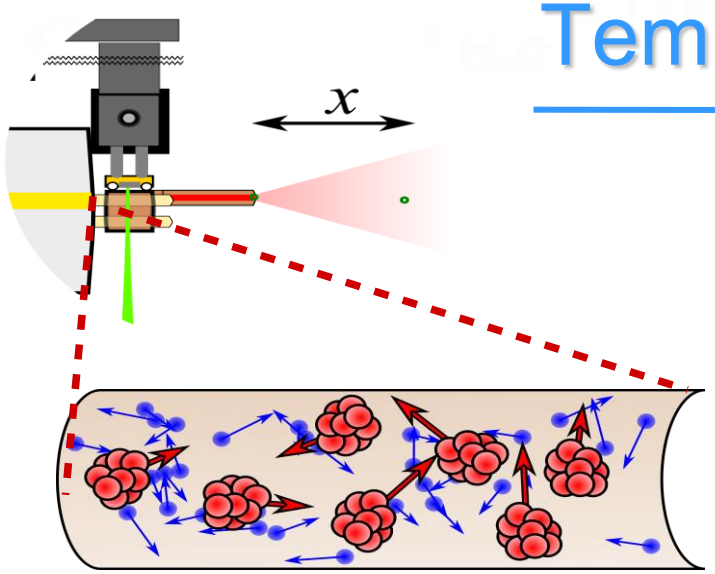
What is the temperature of clusters in a molecular beam

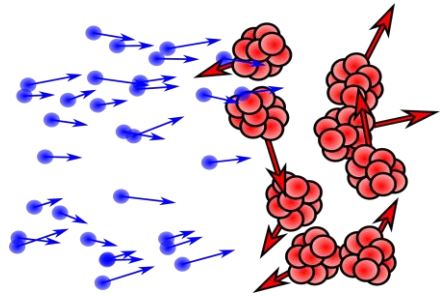
- Creation of atoms is violent process (plasma, laser, oven, discharge)
- Many collisions in source → heat exchange from source body with clusters via carrier gas. But counteracted by heating due to growth (binding energy). Is thermalization complete?
- Expansion in vacuum → cooling, but how much? Cf. size-dependent velocity slip.
- Possible differences in translational, vibrational (not efficiently cooled in expansion), rotational temperature possible.

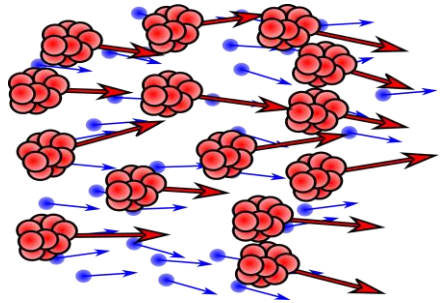


Temperature in a molecular beam





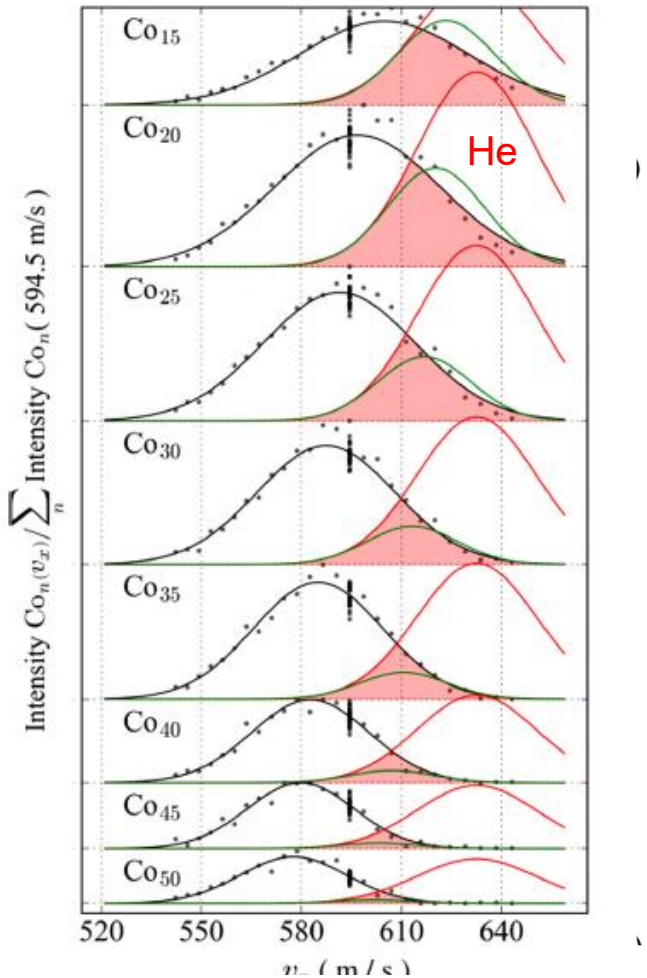


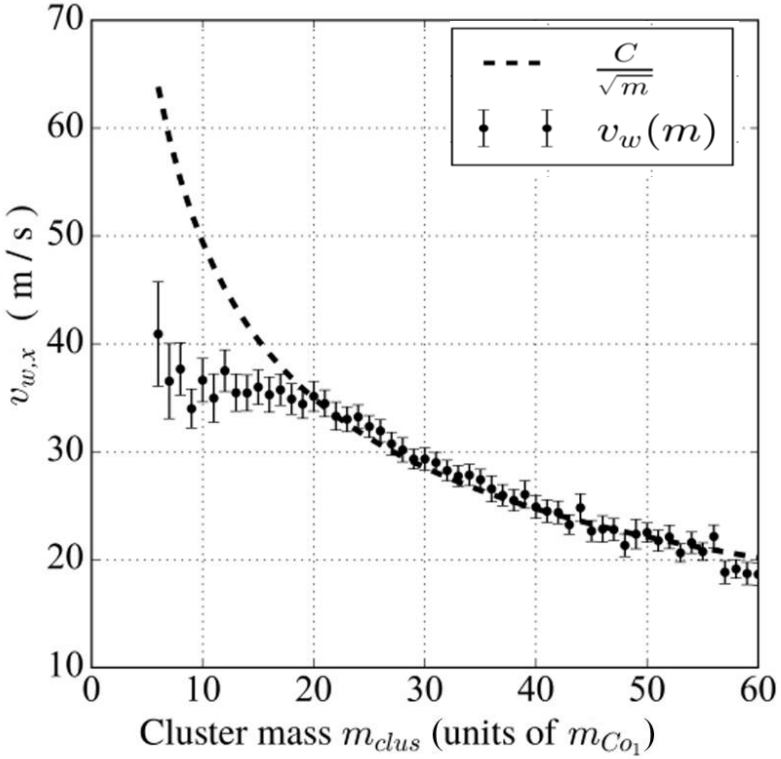


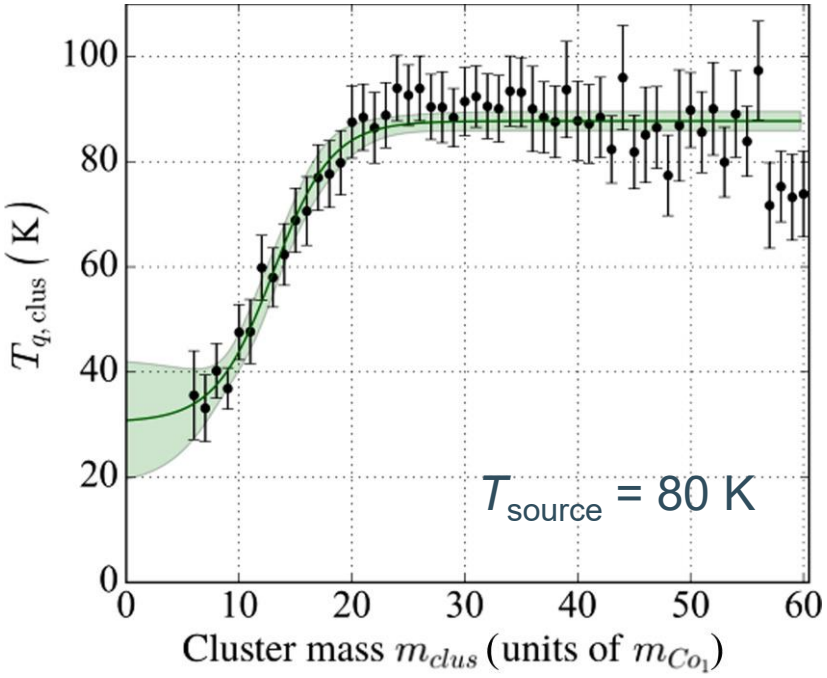
- Light He gas undergo stronger **expansion** (and cooling) that heavy clusters.
- He-cluster collision will on average accelerate clusters, so that their velocity distribution comes closer to that of He.
- But coupling is incomplete = **velocity slip**. Slip is larger for heavier clusters.
- Demonstrated by measurement of the **velocity distributions** as function of cluster size. Width of this distribution increases with temperature.

J. van der Tol, E. Janssens, *Size-dependent velocity distributions and temperatures of metal clusters in a helium carrier gas*, Phys. Rev. A **102**, 022806 (2020)

Temperature in a molecular beam







$$f(v_x)dv_x \propto \exp\left(-\frac{(v_x - w)^2}{{v_{w,x}}^2}\right)dv_x$$

$$v_{w,x} = \sqrt{\frac{2kT_x}{m}}$$

Large clusters have same temperature as source block → thermalized in source and basically no cooling in expansion.

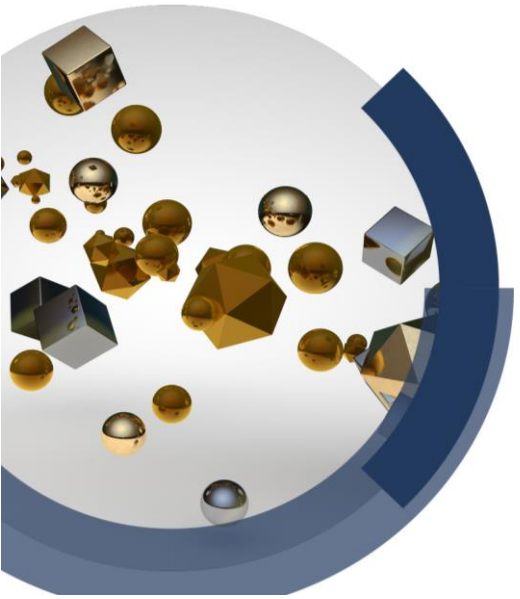
Small clusters have lower temperature → cooled by expanding He gas

Conclusion

- **Gas aggregation sources** are **versatile tools** to grow clusters/nanoparticles/nanoalloys with different sizes, composition, chemical order….
- Some **insight** in the **working principles** and particle **growth mechanisms** has been obtained, but to be able to fully exploit their potential more (experimental and simulation) research is required.
- Yields are sufficient for research purposes, but to use them for technological applications (should that be envisaged) **scaling up** is needed.

Additional reading

- Webinar by Yves Huttel on PhysicsWorld (Oct 2021) https://physicsworld.com/a/past-present-and-the-future-of-gas-aggregation-sources-for-nanoparticle-synthesis/
- Book: *Gas-phase synthesis of nanoparticles* edited by Y. Huttel (Wiley-VCH, 2017)
- P. Ferrari, G. Sanzone, J. Yin, E. Janssens, *Physical synthesis of nanoalloys* in *Nanoalloys: from fundamentals to emergent applications,* editor F. Calvo (Elsevier, 2020)
- P. Grammatikopoulos, S. Steinhauer, J. Vernieres, V. Singh, M. Sowwan, *Nanoparticle design by gas-phase synthesis*, Adv. Phys. X **1**, 81 (2016)
- Y. Huttel, L. Martínez, A. Mayoral, I. Fernández, *Gas-phase synthesis of nanoparticles: present status and perspectives*, MRS Communications **8**, 947 (2018)
- E. Palmer, R. Cai, J. Vernieres, *Synthesis without solvents: The cluster (nanoparticle) beam route to catalysts and sensors*, Acc. Chem. Res. **51**, 2296 (2018)
- G. Sanzone, J. Yin, H. Sun, *Scaling up of cluster beam deposition technology for catalysis application*, Front. Chem. Sci. Eng. **15**, 1360-1379 (2021)

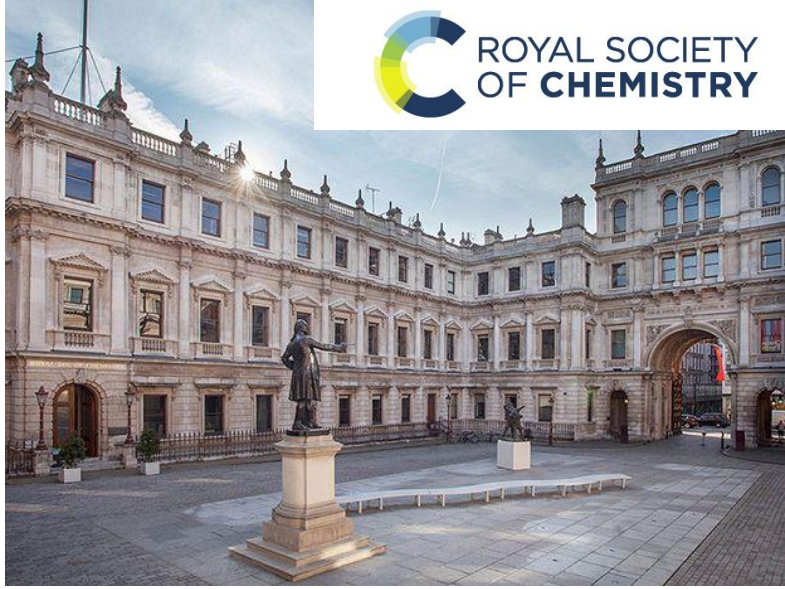


Nanoalloys:
Recent developments and future perspectives

Faraday discussion

21-23 September 2022, London, UK
rsc.li/nanoallos-fd2022

Poster abstract deadline: 11/07/22
Early bird registration deadline: 01/08/22
Registration deadline: 22/08/22



ROYAL SOCIETY OF CHEMISTRY

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Nanoalloy structures
Nanoalloy catalysis
Magnetic and optical properties of nanoalloys
Applications of nanoalloys

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