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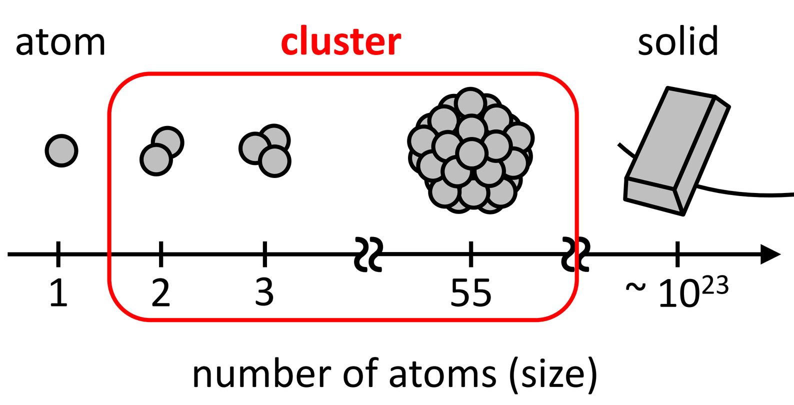
Formation of Metal Cluster Ion Beams Investigated by Mass Spectrometry and Optical Emission Spectroscopy[1]

○ Satoshi Kono, Masashi Arakawa, and Akira Terasaki (Department of Chemistry, Kyushu University, Japan)

Introduction

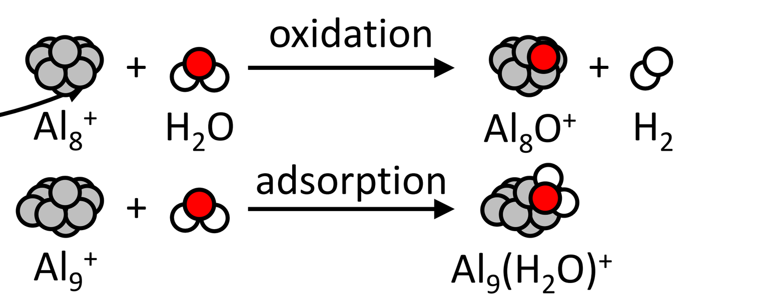
◆ About "Cluster"

★ **Definition** … aggregates of several to several hundreds of atoms.



★ **Feature** … **size-dependent properties**

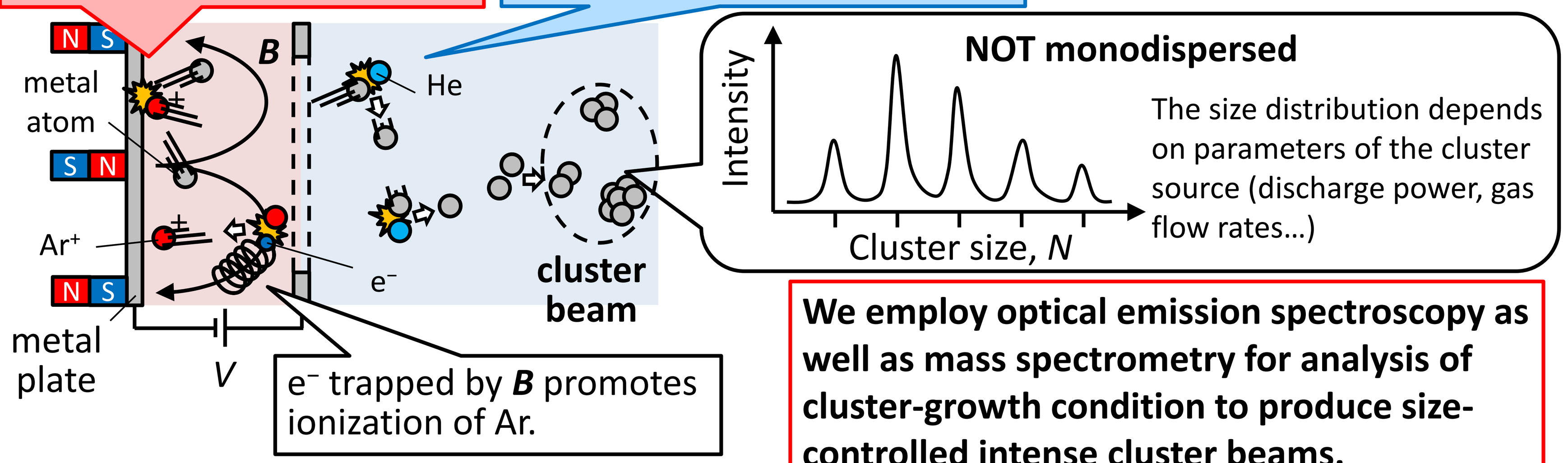
e.g. reaction of aluminum cluster cation (Al_N^+) with water[2]



◆ Magnetron Sputtering Method[3] … one of the methods for cluster generation

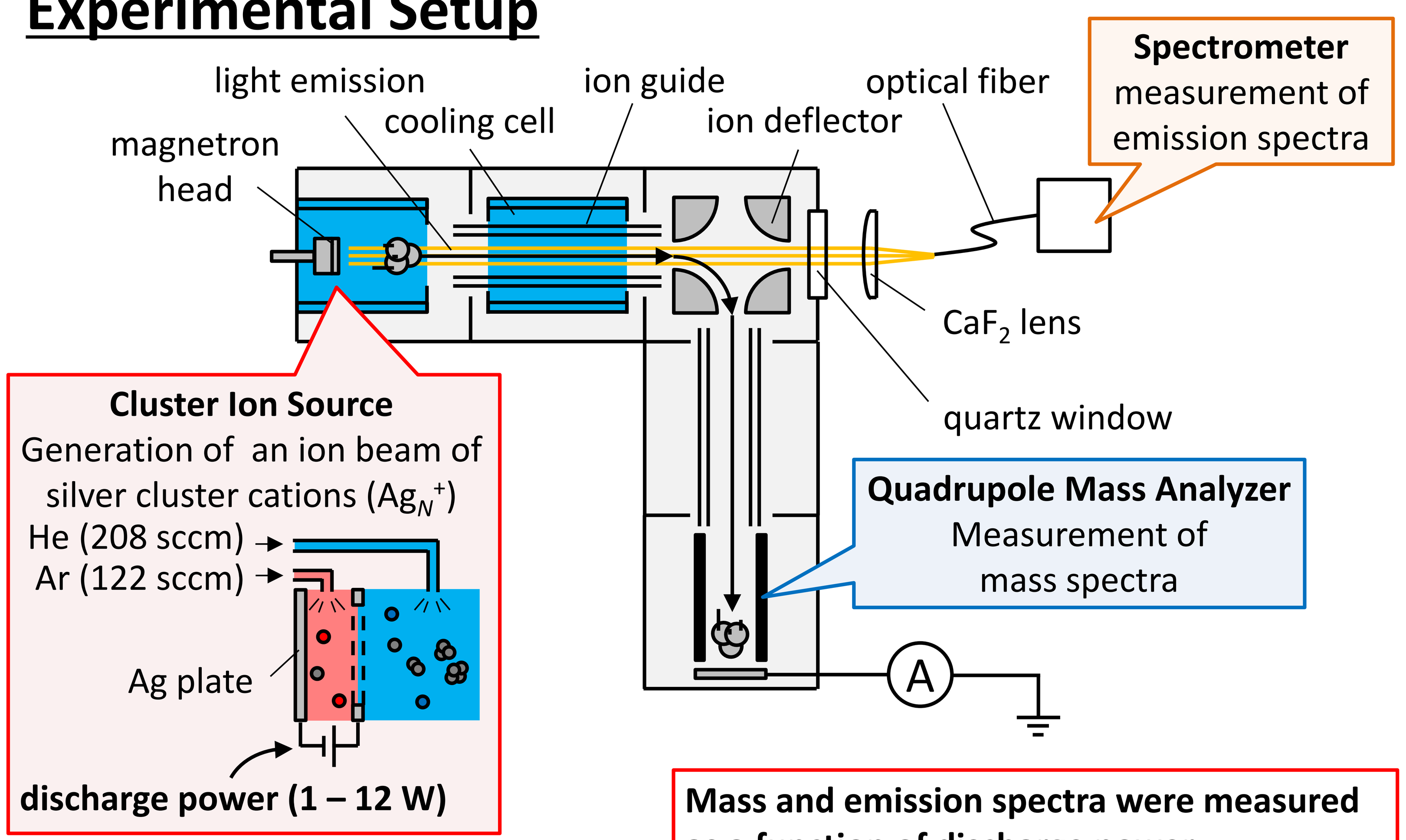
(1) An Ar gas ionized by discharge sputters the plate

(2) Metal atoms aggregate by collision with a cold helium gas



We employ optical emission spectroscopy as well as mass spectrometry for analysis of cluster-growth condition to produce size-controlled intense cluster beams.

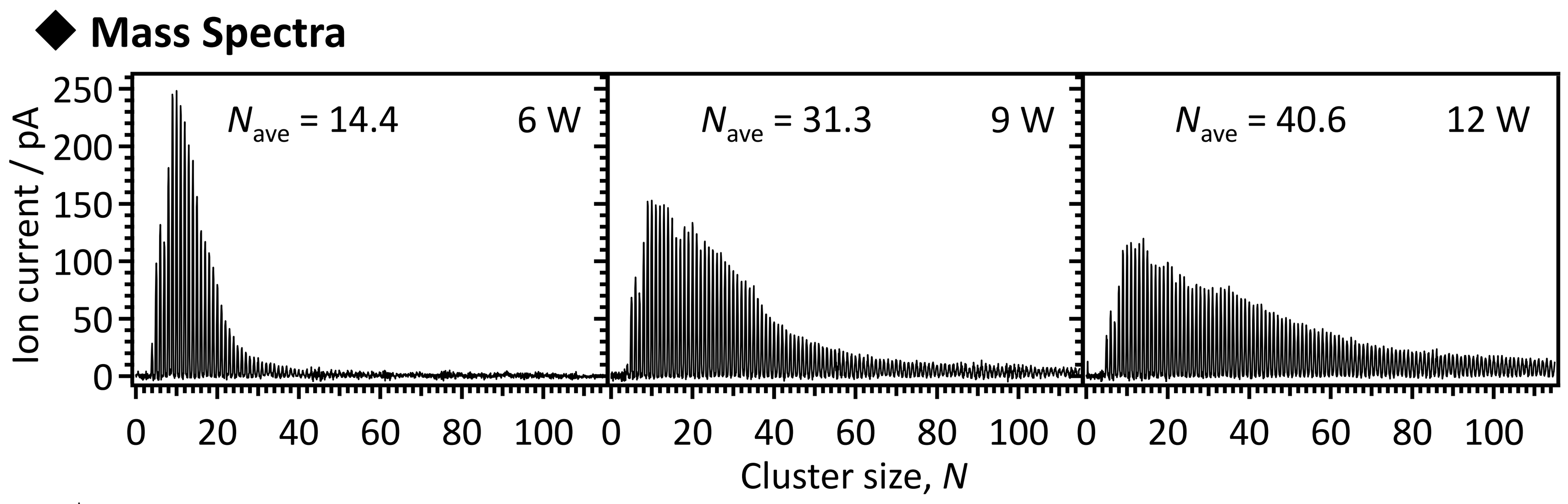
Experimental Setup



Mass and emission spectra were measured as a function of discharge power.

Results

◆ Mass Spectra



★ **Mass distribution shifted to larger sizes as discharge power increased.**

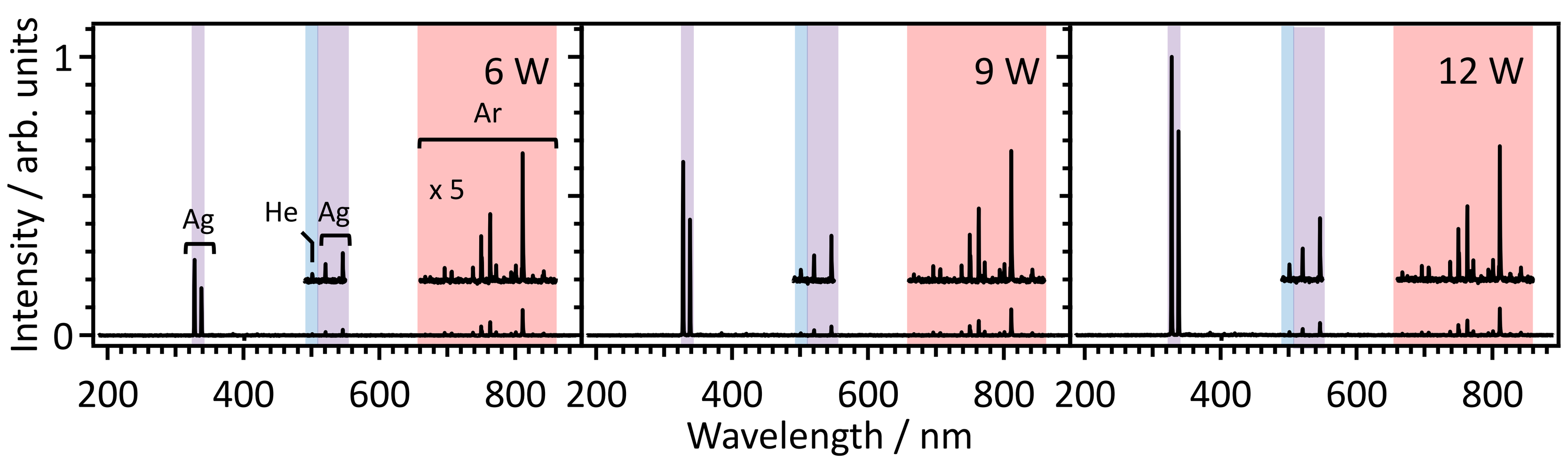
Here the average cluster size, N_{ave}, was evaluated by the following equation:

$$N_{ave} = \sum_{N=1}^{115} i_N N \Big/ \sum_{N=1}^{115} i_N ,$$

i_N: current of Ag_N^+

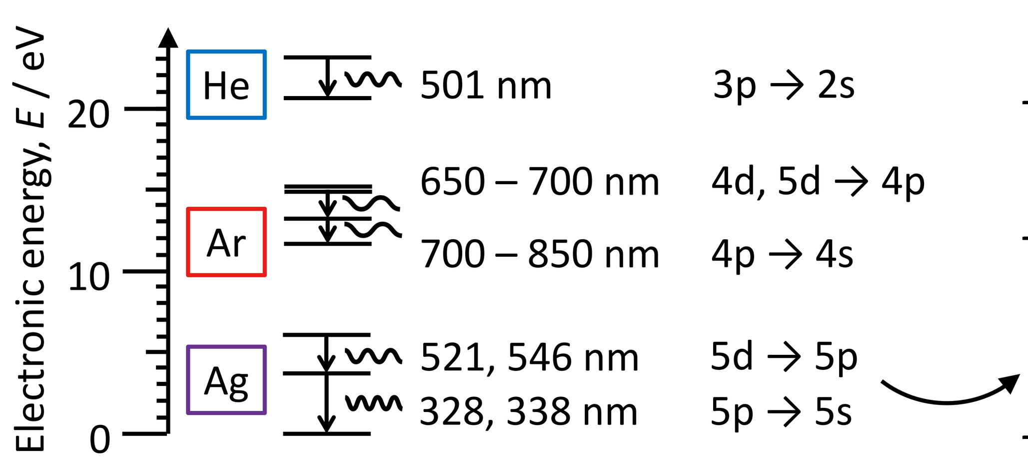
Measurable size range was limited up to 115 due to the setup.

◆ Emission Spectra



★ **The intensity of Ag lines increased as discharge power increased, indicating an increase in the amount of Ag atoms.**

★ **Assignment of Emission Lines** … referring to the NIST Atomic Spectra Database[4]



Wavelength / nm	Einstein A coefficient, A / 10^8 s^{-1}	Transition
328	1.4	$^2P_{3/2} \rightarrow {}^2S_{1/2}$
338	1.3	$^2P_{1/2} \rightarrow {}^2S_{1/2}$
521	0.75	$^2D_{3/2} \rightarrow {}^2P_{1/2}$
546	0.86	$^2D_{5/2} \rightarrow {}^2P_{3/2}$

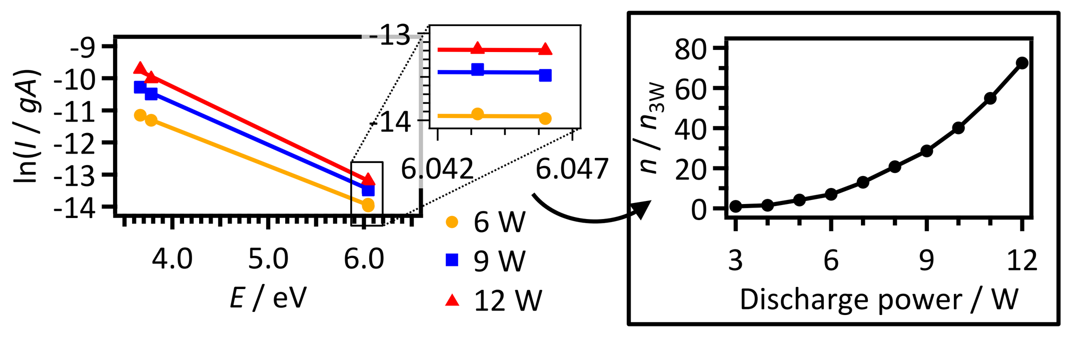
Discussion

◆ Evaluation of the Amount of Ag atoms, *n*

Emission intensity, I, should be proportional to the number of atoms, n, assuming that population of excited states follows the Boltzmann distribution:

$$I = \alpha g A n \exp\left(-\frac{E}{kT}\right) \rightarrow \ln\left(\frac{I}{gA}\right) = -\frac{E}{kT} + \ln(\alpha n)$$

Relative values of *n* can be evaluated.

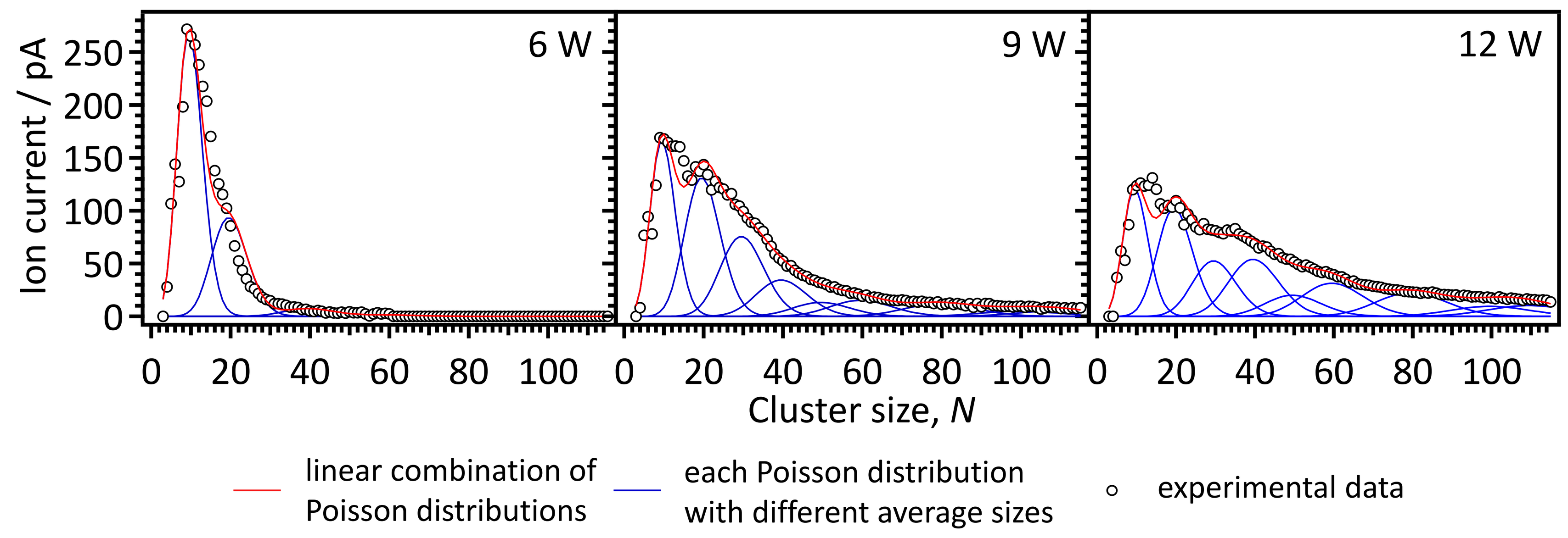


I: emission intensity
g: statistical weight of the initial state
k: Boltzmann constant
T: temperature
α: coefficient to convert the emission rate to the intensity.

◆ Analysis of Mass Spectra

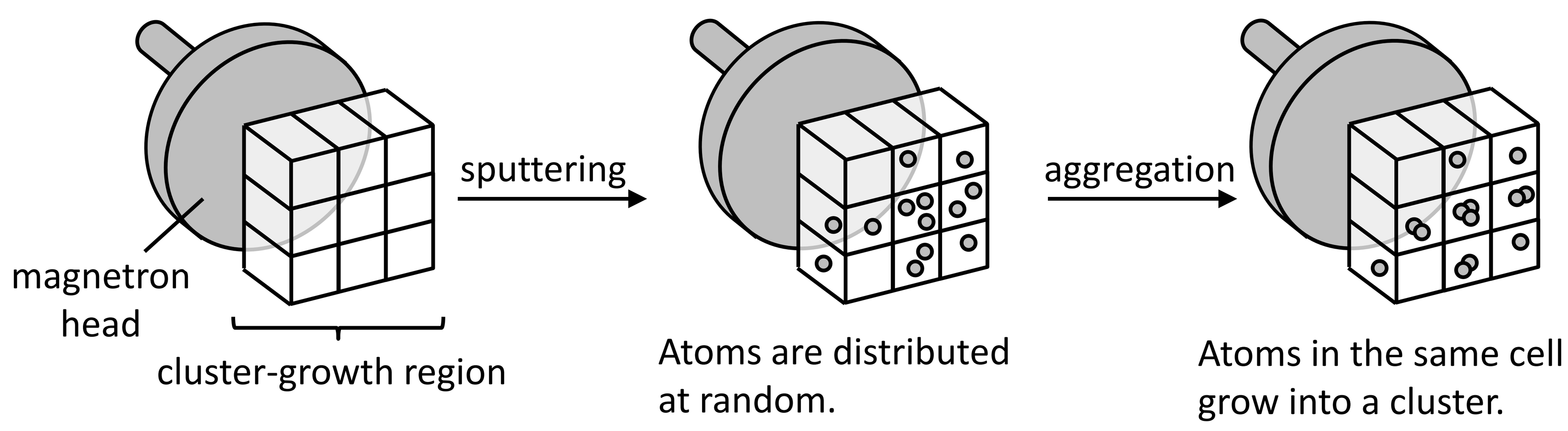
We tried to find out the size-distribution function that explains the experimental data.

→ The spectra were reproduced by linear combination of Poisson distributions with several different average sizes.



◆ Lattice Model for Cluster Formation

To explain the result of mass spectroscopic measurements, we propose a lattice model:



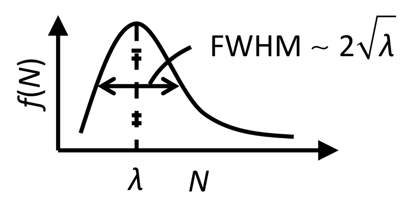
◆ Analysis of the Cluster Source based on the Model

★ **Size-distribution of clusters produced**

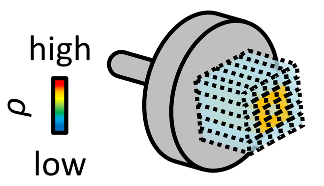
The size distribution $f(N)$ follows a **Poisson distribution**.

$$f(N) = \frac{\lambda^N e^{-\lambda}}{N!}$$

λ: average cluster size ∝ density of sputtered atoms

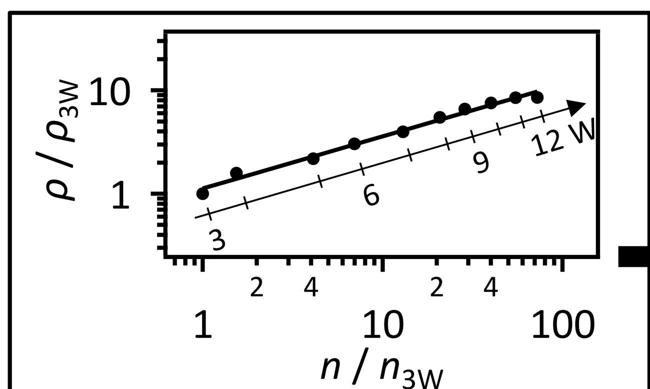


→ **The combination of multiple distributions rather than a single distribution implies inhomogeneity in the density of Ag atoms.**



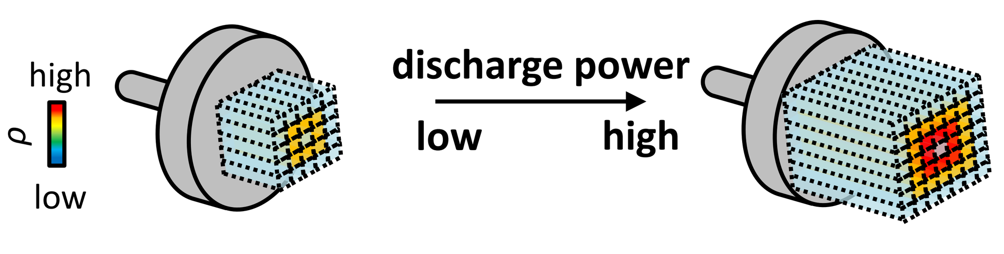
★ **Relationship between the Density and the amount of Ag Atoms**

We compared the density of Ag atoms, ρ (∝ N_{ave}) with the amount of sputtered Ag atoms, n.



ρ is NOT proportional to n, but rather to $\sqrt{n}$

The volume of cluster-growth region enlarges as the discharge power is raised



This result suggests that one should keep the volume small at high power for generating a large metal-cluster beams.

Summary

We investigated formation of metal-cluster ion beams by optical emission spectroscopy as well as by mass spectrometry.

◆ **We propose a lattice model for cluster formation**, which can reproduce size-distribution of clusters by assuming **inhomogeneous density distribution of silver atoms**.

◆ We found that the **cluster-growth region enlarges** at high discharge power, which resulted in suppression of cluster growth.

References

[1] S. Kono et al., *Chem. Lett.* **2019**, *48*, 1537.
[2] M. Arakawa et al., *Eur. Phys. J. C* **2013**, *67*, 80.
[3] H. Haberland et al., *J. Vac. Sci. Technol. A* **1992**, *10*, 3266.
[4] NIST, Atomic Spectra Database, https://www.nist.gov/pml/atomic-spectra-database