Aerosol Dynamics in Sputtering DC discharge

A. Michau[1], K. Hassouni[1], C. Arnas[2], G. Lombardi[1]

[1] LSPM, Université Paris 13, Sorbonne Paris Cité, Laboratoire des Sciences des Procédés et des Matériaux, CNRS (UPR 3407), F-93430 Villetaneuse, France

[2] LPIIM, Aix-Marseille université, CNRS, Campus Saint Jérôme, 13397 Marseille, France

14th Workshop on the Physics of Dusty Plasmas

Outline

Develop a numerical model describing solid carbon nanoparticle formation and behaviour in an Argon DC discharge

- ➢ Molecular growth
- ➢ Particle nucleation and growth

- How particles are produced ?

- What are the mechanisms for the particle growth ?

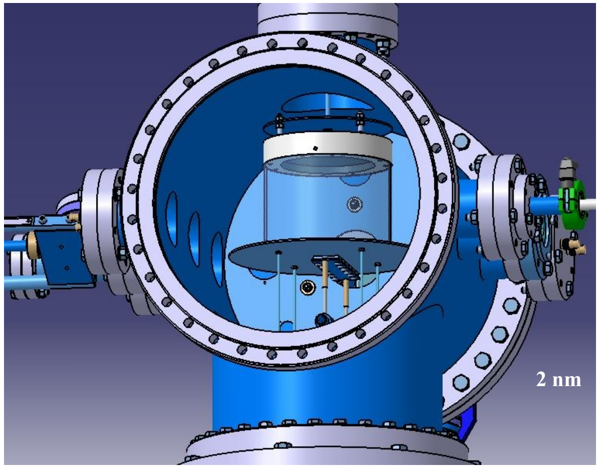
Assumption : no dusty plasma effect

Experiment developed at PIIM-France (C. Arnas)

Experiment

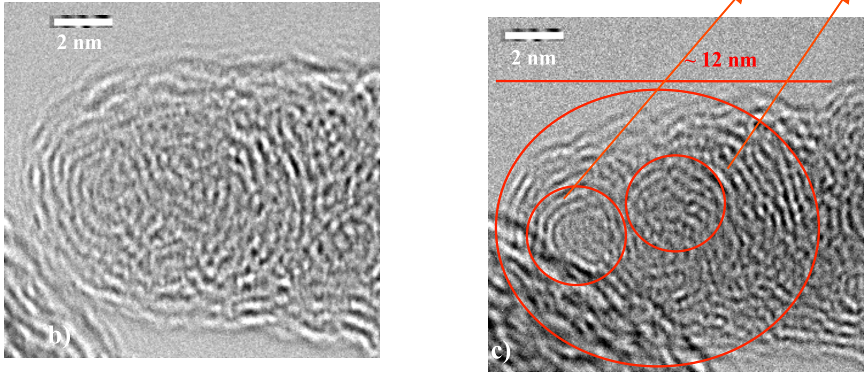
Argon DC Discharge - graphite Cathode

C. Arnas PIIM



- **Conditions**
  - **A 14 cm gap**
  - **voltage V_d ~ - 600 V**
  - **Current = 80 mA**
  - **Pressure = 0.6 mbar**
  - **Discharge Duration 5 mn**
  - **Volume ~1 L**

TEM Images of a 12 nm particle
produced after a 60 s plasma discharge



2 nucleides
of 2-3 nm

- Quasi spherical Particles
- Growth by coagulation and molecular sticking

T_{growth} ~ 100.$T_{diffusion}$ electrostatic trapping of charged species

Model schematic (1D)

- Trapping mechanism that enables long residence time → Plasma module
- Nucleation of particle results from molecular growth → Cluster module
- Molecular sticking on particles
- Aerosol dynamics → Aerosol Module

Coupling

Solution Scheme adopted

Plasma module
+
Cluster module
+
Averaged Particle Module

Input →

•Ne, E,
•Nucleation rate,
•Clusters densities

Sectional Aerosol Module

Plasma model

1. **Kolobov and Tsendin Sheath dynamic model combined with a Monte Carlo simulation** Kolobov & Tsendin, Phys. Rev. A **46** 7837 (1992)

   -> Sheath dimension & Non local ionization source term $S_i(x)$

2. **Ambipolar diffusion equation for the cold electron population**

$$-D_a \frac{d^2 n_e}{dx^2} + \frac{n_e}{\tau} = S_i(x) \qquad D_a = f(T_e, T_{ar+}, D_{ar+})$$

3. **Boltzmann distribution for the cold electrons**

   -> determination of the very small ambipolar field in the NG/FDS

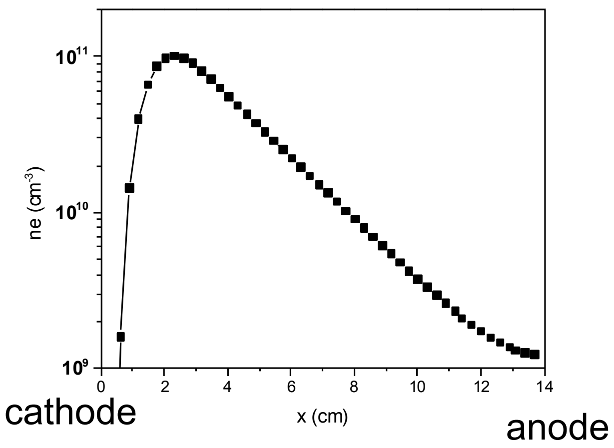
$$n_e = n_e^0 e^{\frac{\phi}{kT_e}}$$

$$E = -\frac{kT_e}{e}\nabla \ln(n_e)$$

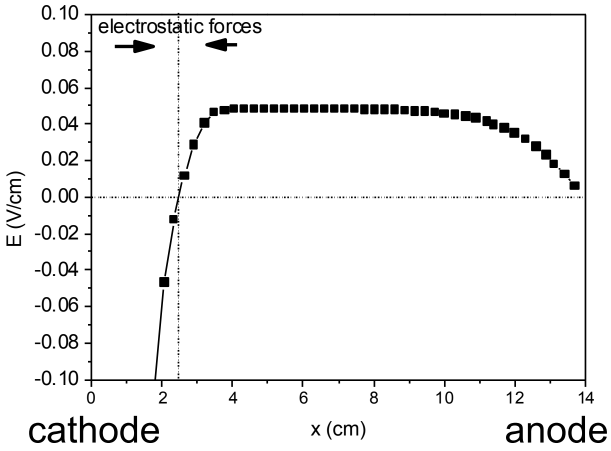
Model Parameter : Te

Plasma characteristics

Electron Density



Electric Field



- Electron density in good agreement with experimental results
- High density for 1-4 cm from the cathode – strong decrease in FDS

- E-inversion at 2 cm from the cathode.
- Electrostatic confinement on negative species at this position

Cluster Model

Only neutral and negative clusters from C_1 to C_{30}

- transport
- Growth by aggregation
- Attachment / detachment/charge exchange
- Radial losses
- Losses by sticking on particles
- Losses by nucleation

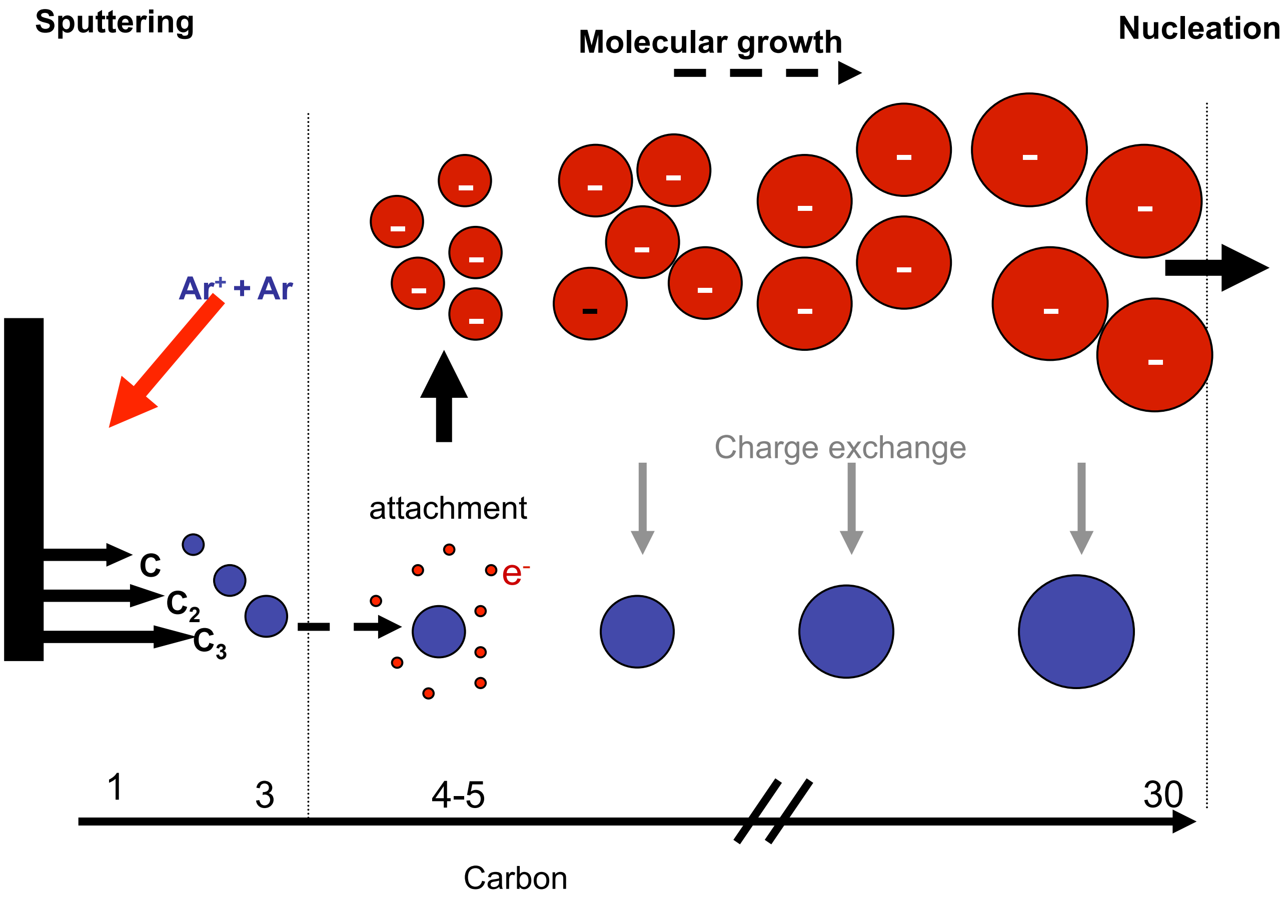
} Coupling with particle module

Density balance

$$\frac{\partial n_i^z}{\partial t} = -\nabla(-D_i\vec{\nabla}n_i^z + \mu_i.z.\vec{E}) + W_i^z - P_i^r$$

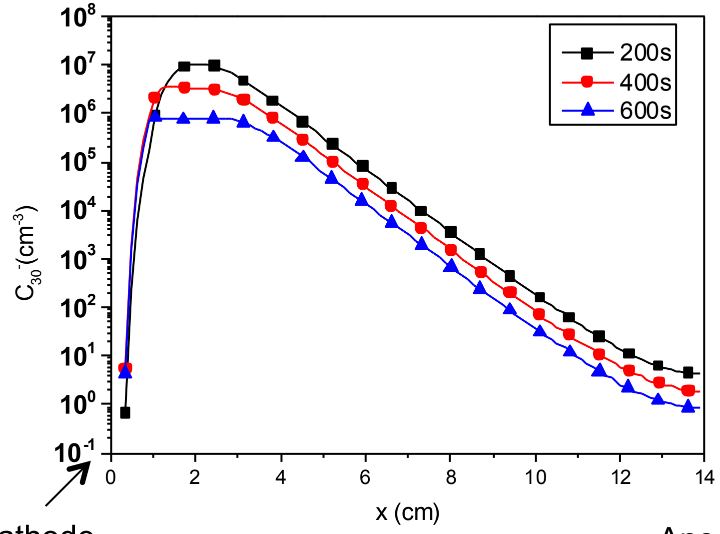
i=1,63 z=0,-1

Cluster growth schematic



Nucleation

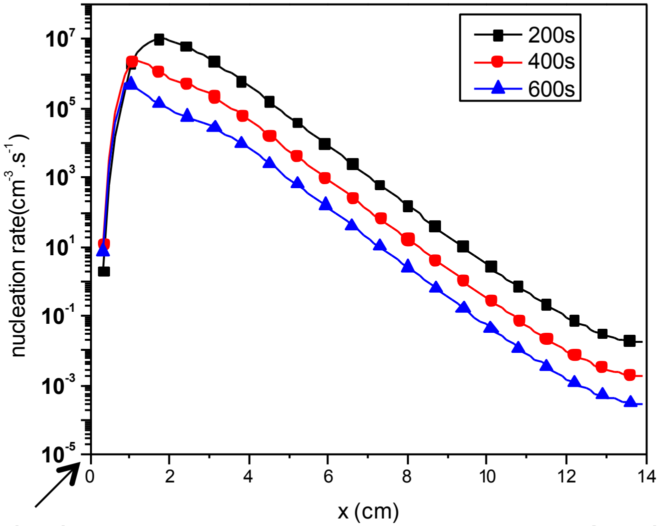
Largest negative cluster density



Cathode Sputtering

Anode

Nucleation rate

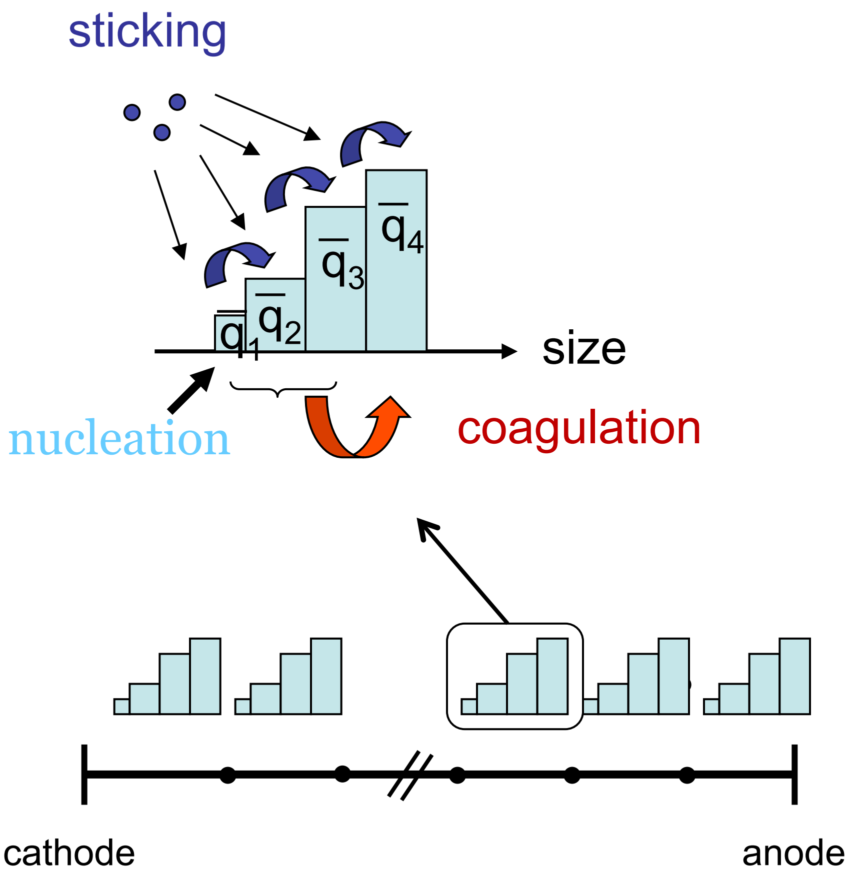


Cathode Sputtering

Anode

- Nucleation due to growth of C_{30}^{-}
- Particle nucleation remains during all discharge duration
- Decrease of nucleation rate due to consumption of clusters sticking on existent particles

Aerosol Model : Particle Volume



- Nucleation
- transport
- Growth by sticking
- Growth by coagulation

Volume balance

$$\frac{\partial Q_l(t)}{\partial t} = \left.\frac{\partial Q_l(t)}{\partial t}\right|_{coag} + \left.\frac{\partial Q_l(t)}{\partial t}\right|_{sticking} + S_{nucleation} - \nabla F_l$$

Particle size range : 1-100 nm
100 sections

Gelbard *J. of Colloid and Int Sci* **76**, 1980
Warren *Aerosol Sci and Tech*, 4 1985

Aerosol Model : Particle Charge

$$\boxed{k_{coag}(q\ ,q') = k_{coag}(0,0).w(q,q')}$$

->need for charge distribution for each section in each point

Solution adopted

Charge balance : averaged particle charge for each section

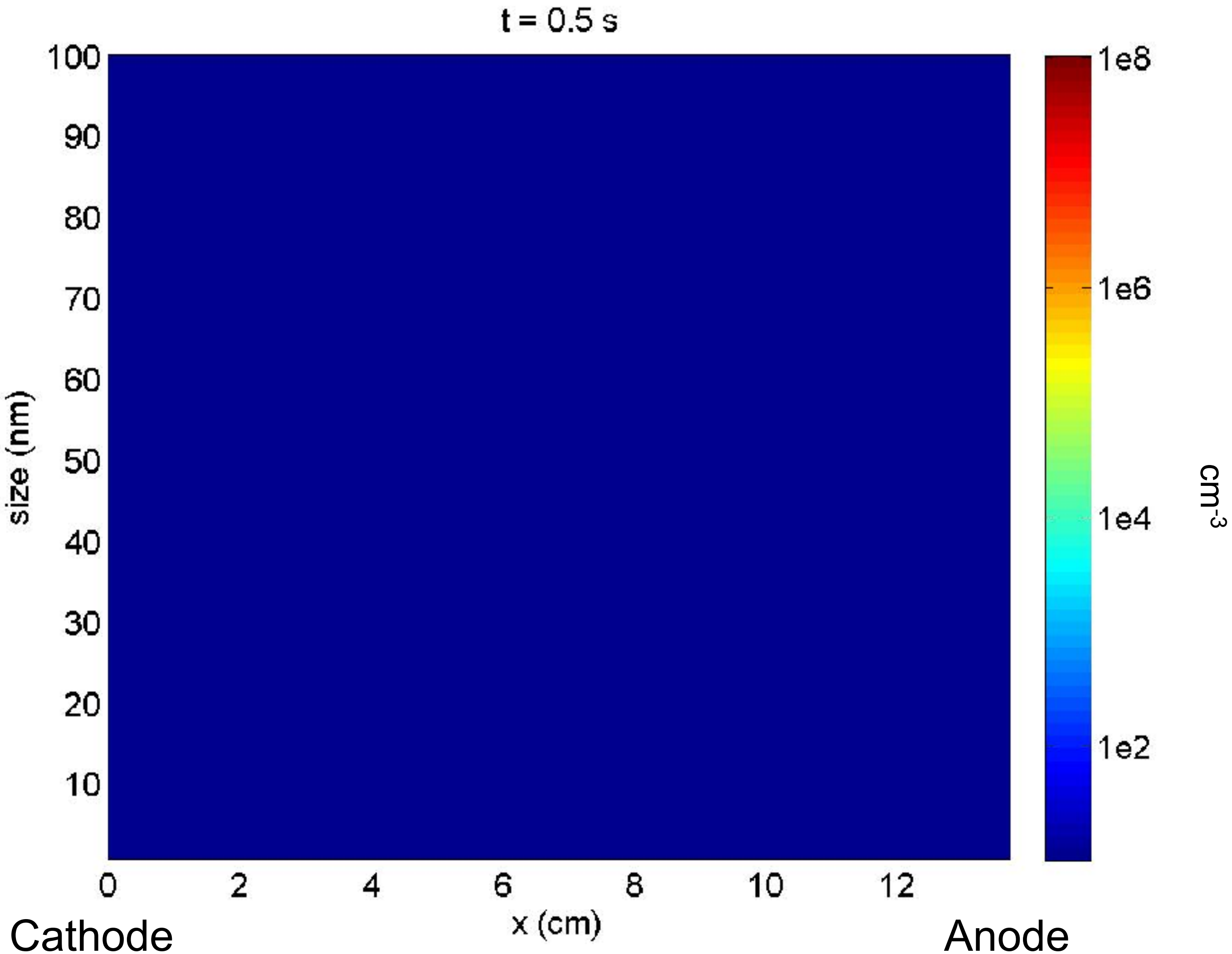
$$\frac{\partial q_l}{\partial t} = -\frac{\vec{\nabla}(q_l \vec{F}_l)}{Q_l} + \left(I_{e-slow} + I_{e-fast} + I_i\right).S_l + S^q{}_{nuc} + S^q{}_{coag} + S^q{}_{sticking}$$

Fluctuation : a fraction of particle could be neutral or positive

$$\psi(q,\bar{q}) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left[-\frac{(q-\bar{q})^2}{2\sigma^2}\right] \qquad \sigma = f\left(\frac{T_e}{T}, q_p, d_p\right)$$

T. Matsoukas, M. Russell, 1995 *Journal of Applied Physics* **77**, p. 4285

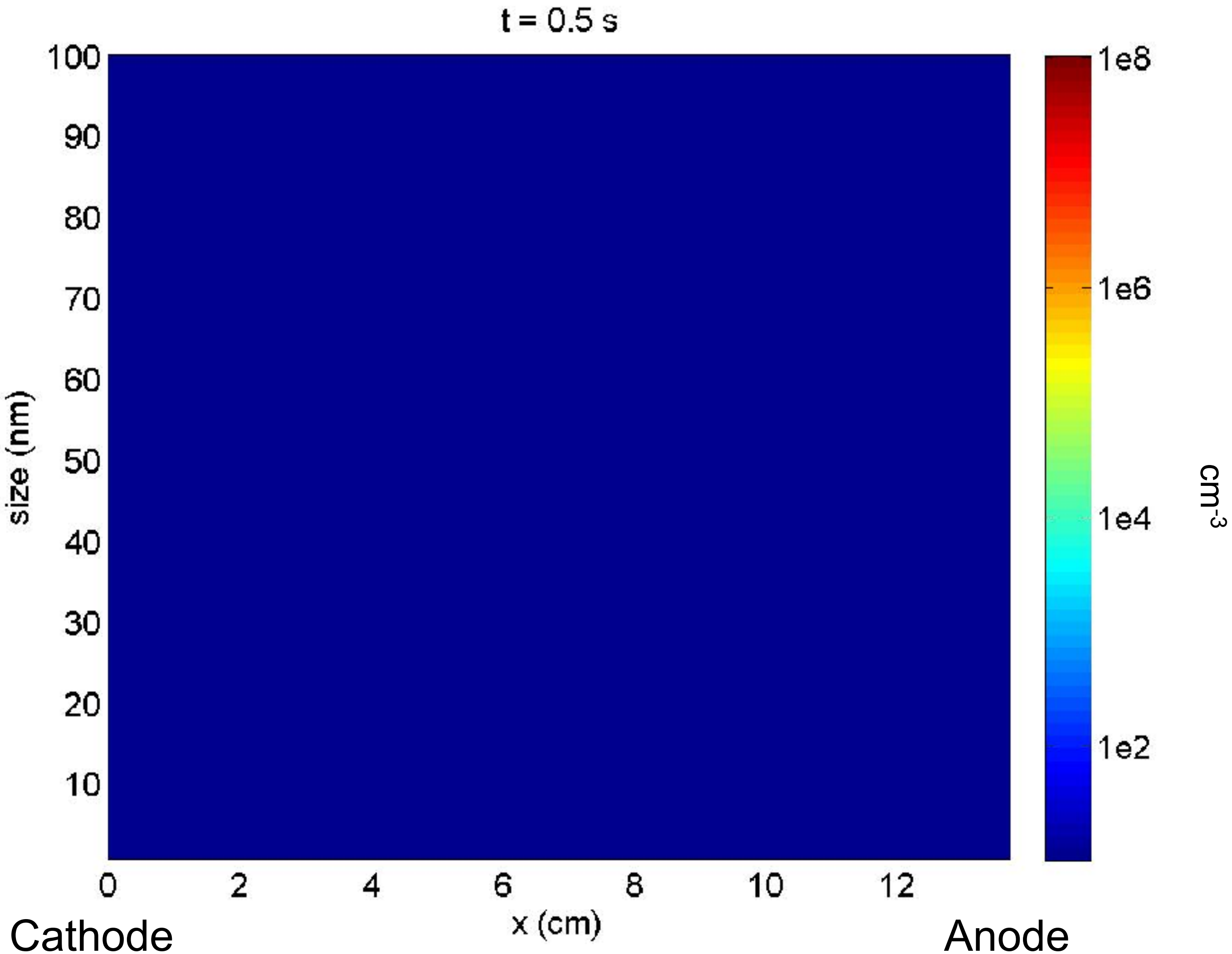
Aerosol Dynamics Results



Cathode

Anode

Aerosol Dynamics Results



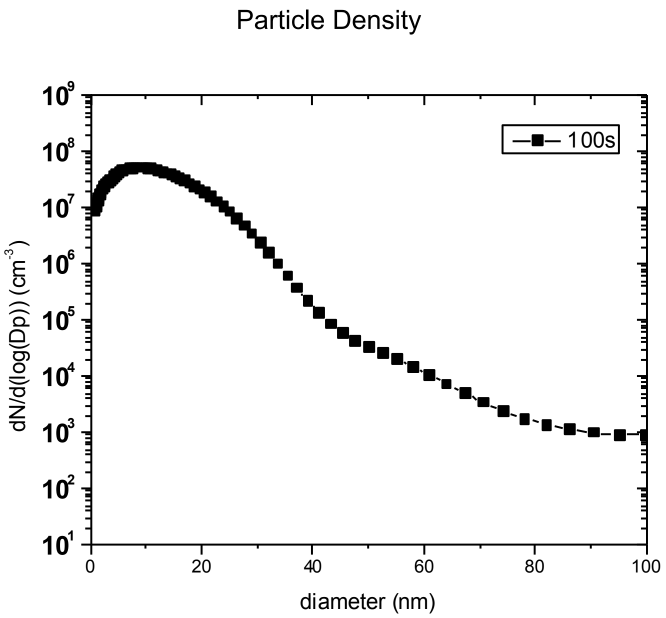
Cathode

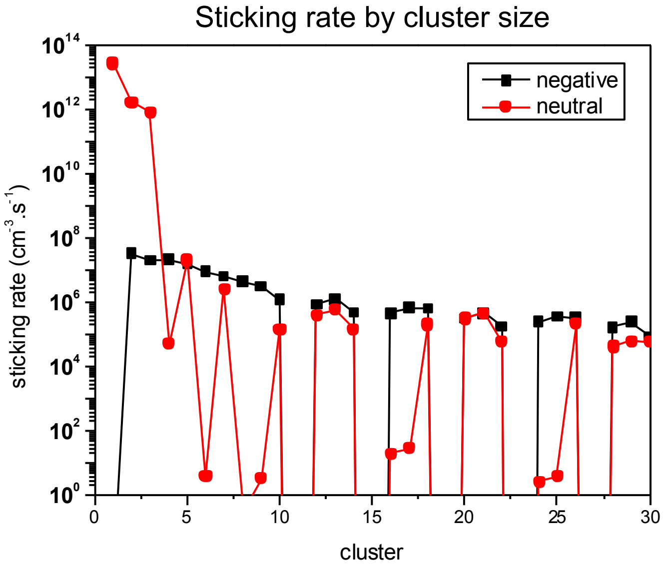
Anode

Particle growth mechanism at 100 s

x= 2 cm

Coutinuous size distribution


Particle Density


Sticking rate by cluster size

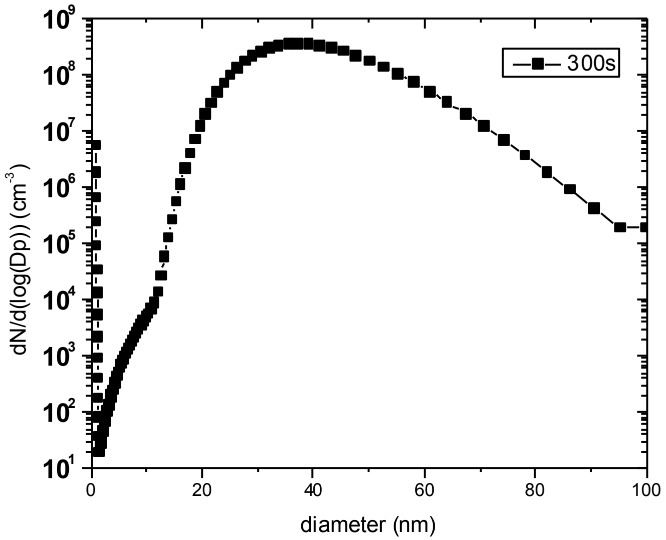
Growth due mainly to molecular sticking

- C, C_2, C_3 from sputtering
- Larger negative cluster sticking possible due to charge fluctuation

Analysis at 300 s

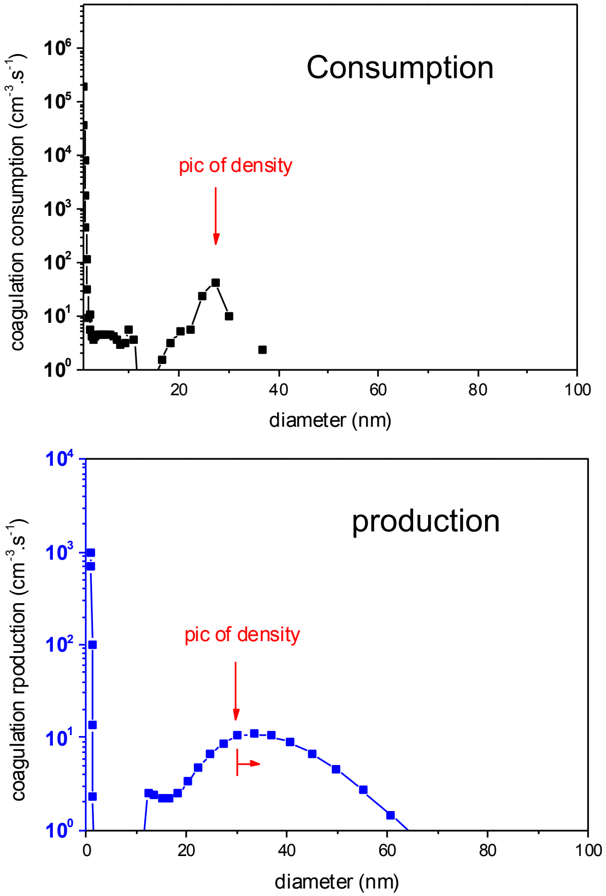
x= 2 cm

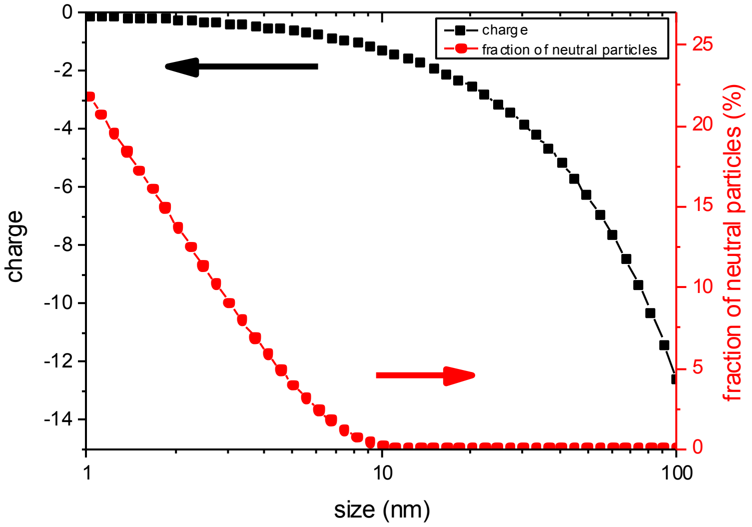
Particle Density



Depletion between 2 and 10 nm

Analysis at 300 s


Coagulation source Term

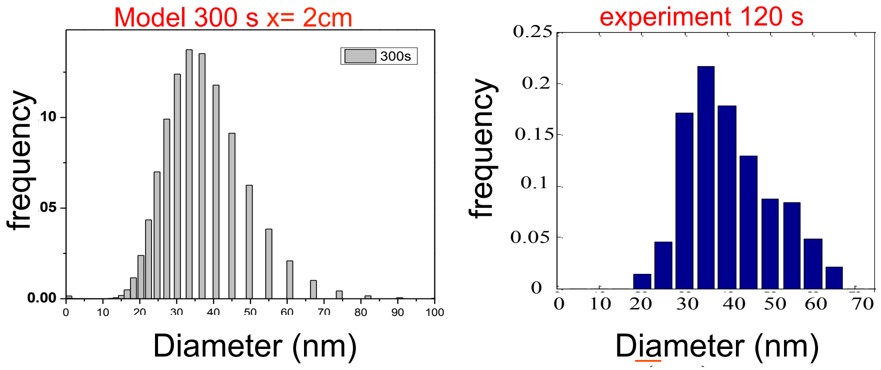

Particle charge distribution

Coagulation = 1 neutral particle of 1-2 nm + 1 negative particle

Comparison with experimental Results

Density : Particle density 10^8 cm^{-3} as experimentally determined

Size distribution : For the same average diameter



d=34 nm d=35 nm

Good agreement at 300 s

Delay may be due to time variation of the sputtering yield

Conclusion

- Our scheme can predict the Particle formation in DC discharge

- Explanation of particle behaviour using sectional model that allow taking into account coagulation involving 1 'small' (<10 nm) particle is predicted

- To extend our model to larger discharge duration and larger particle coagulation :
  - Better resolution of particle charge distribution and fluctuation (dipole)
  - include the ***dusty plasma effect*** by coupling the transport equations of clusters, particle, cold electron and ions along with Poisson's equation for the field.