Turning the Evil into Good: Plasma Synthesis of Silicon Nanoparticles and Potential Applications

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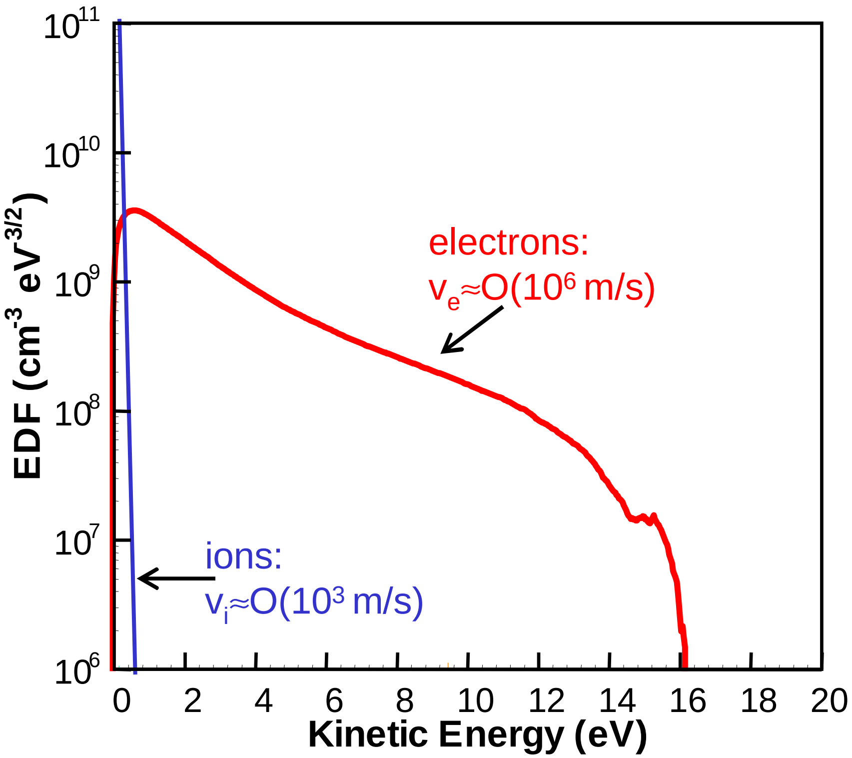
University of Minnesota Supercomputer Institute

Overview

- Introduction
- Single-crystal nanoparticles
- Nanostructured Si:H-films
- Modeling of nanoparticle growth in plasmas

Electrons and Ions

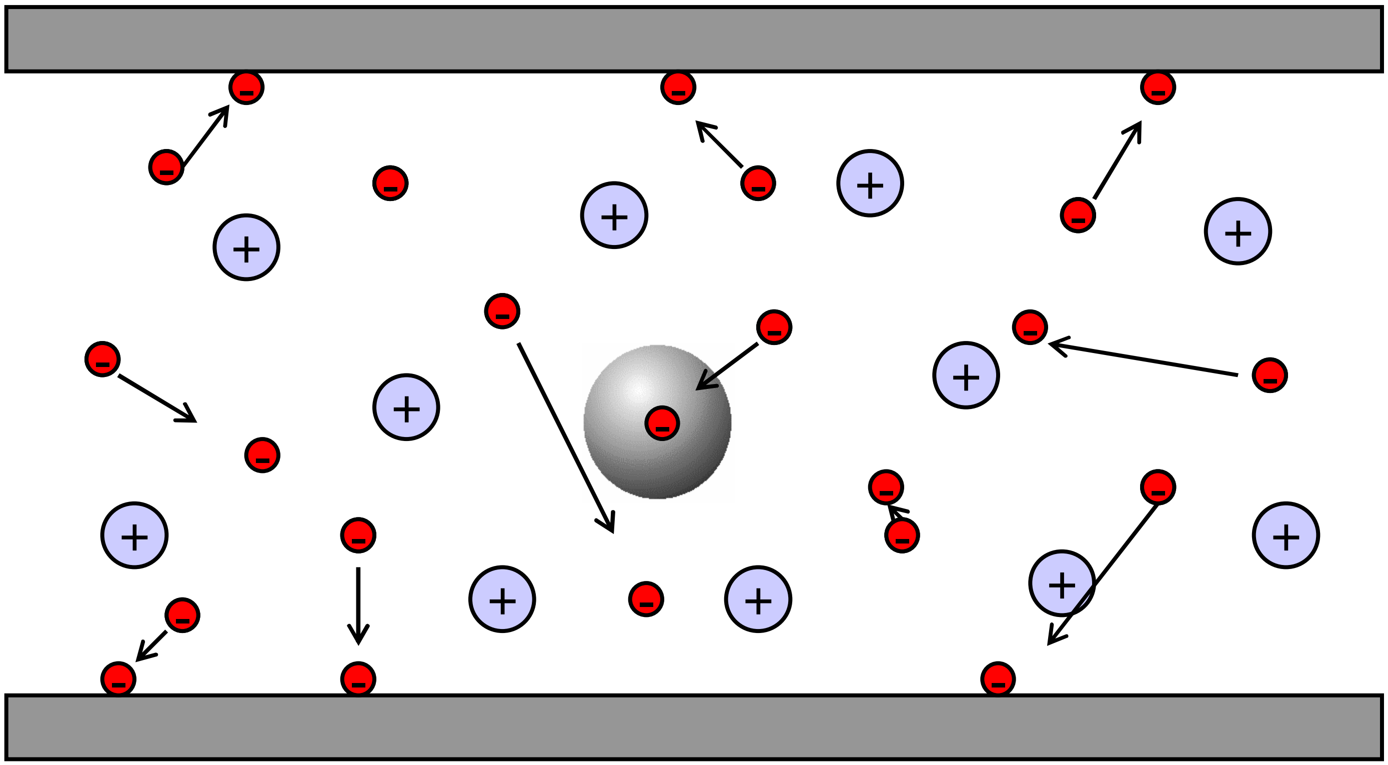


measured EEDF
in Argon Plasma

Low pressure =
Non-equilibrium

- pressure: 1-100 Pa
- $T_{gas} \approx T_i \approx$ 300-2000K
- $T_e \approx$ 20,000-50,000 K (2-5 eV)
- Charge carrier density: $n_i = n_e = 10^9 - 10^{12}$ cm^{-3}

Ambipolar Diffusion



Particles and reactors walls are negatively charged.

Why use LP-Plasmas?

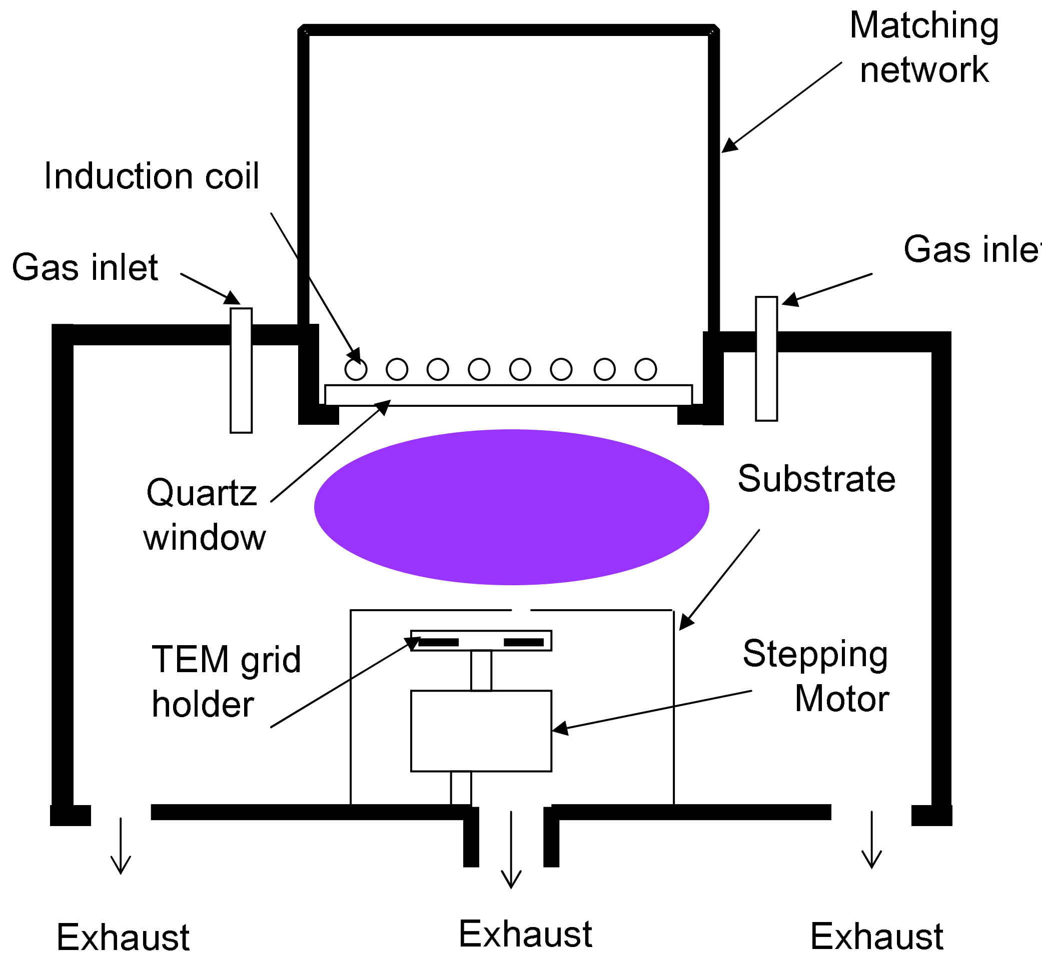
- Reactor walls and particles are negatively charged.
- Particles are confined in the reactor.
- Particles repel each other
  $\Rightarrow$ Coagulation is suppressed.

Single-crystal nanoparticles

A. Bapat[1], C. Perrey[2], Z. Shen[3],
S. Campbell[3], C. B. Carter[2], U. Kortshagen[1]

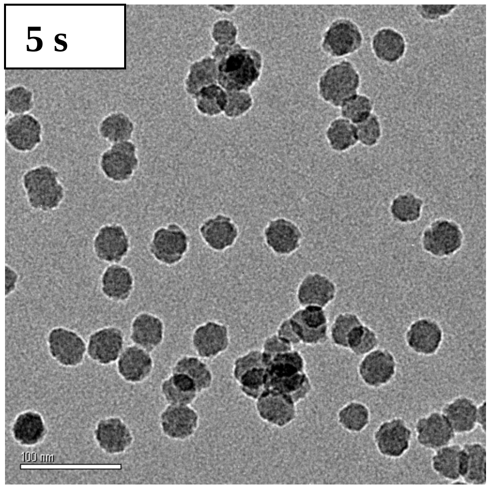
[1]Mechanical Engineering
[2]Chemical Engineering and Materials Sci.
[3]Electical and Computer Engineering

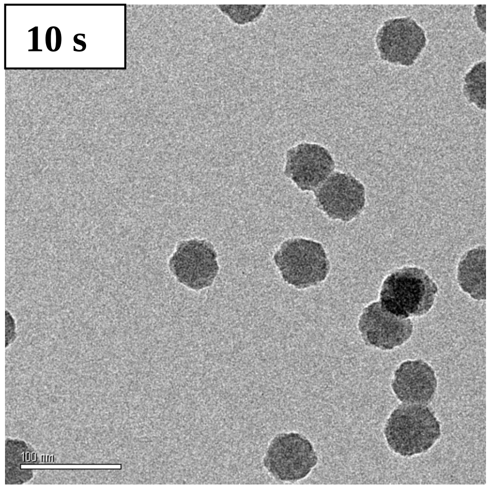
Nanoparticles in inductive plasmas

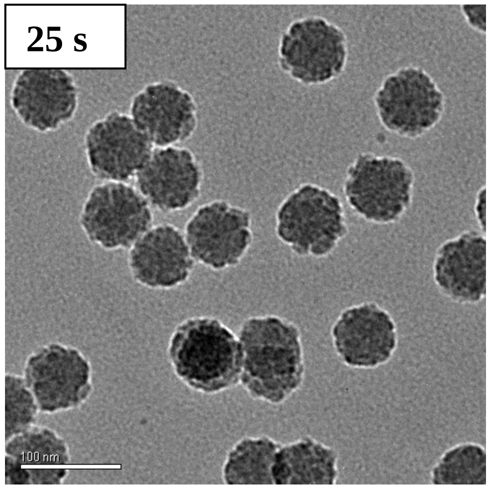


T. Kim, Ph. D. Thesis

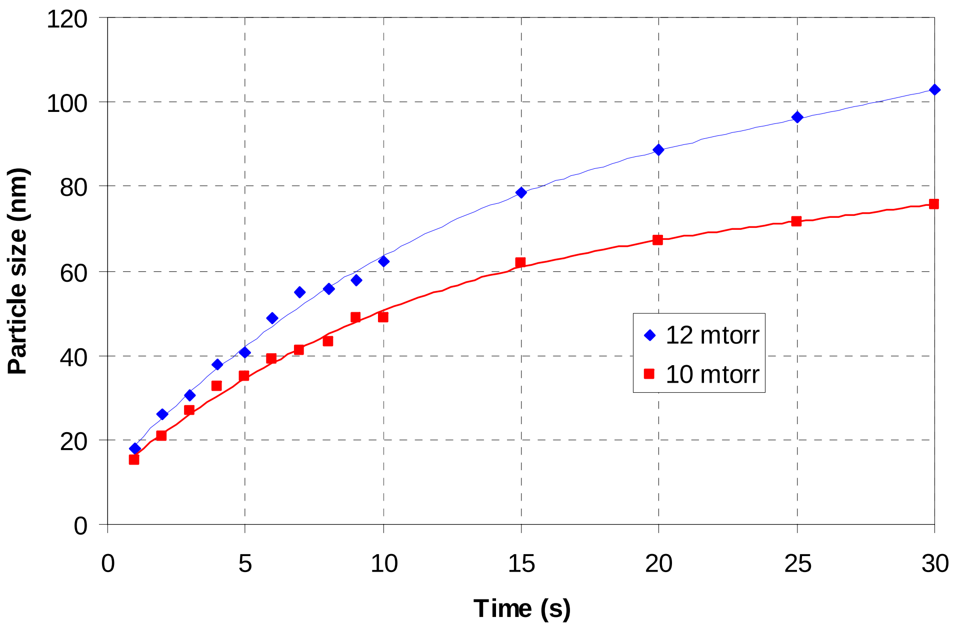
Nanoparticles in inductive plasmas







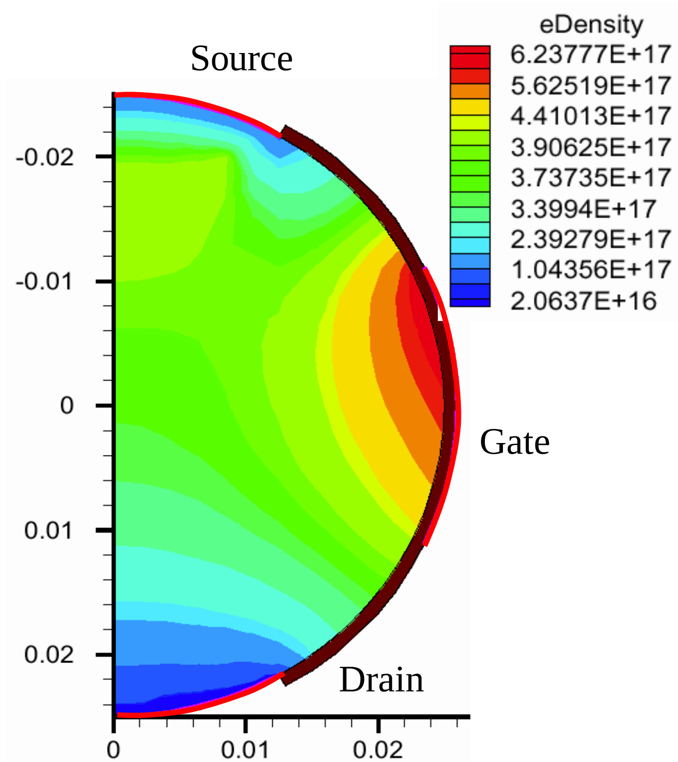
Z. Shen et al., J. Appl. Phys., submitted

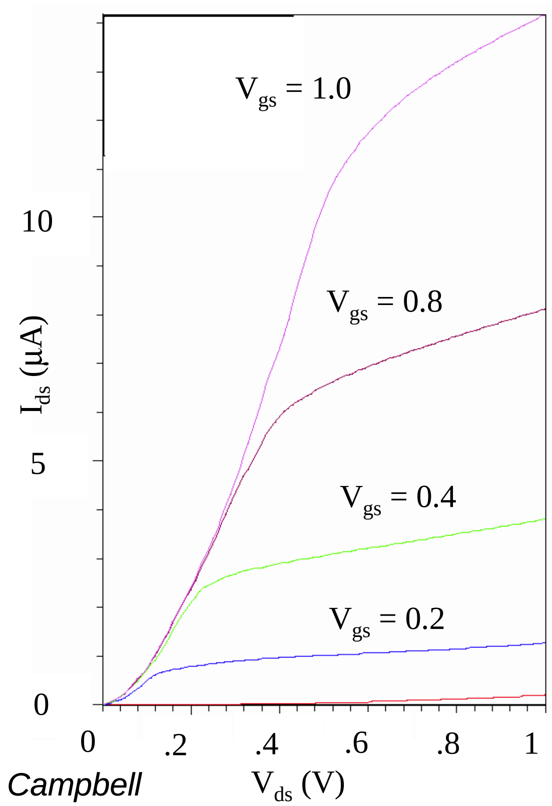


measured

σ_g ~ 1.03-1.1

Science Fiction!!

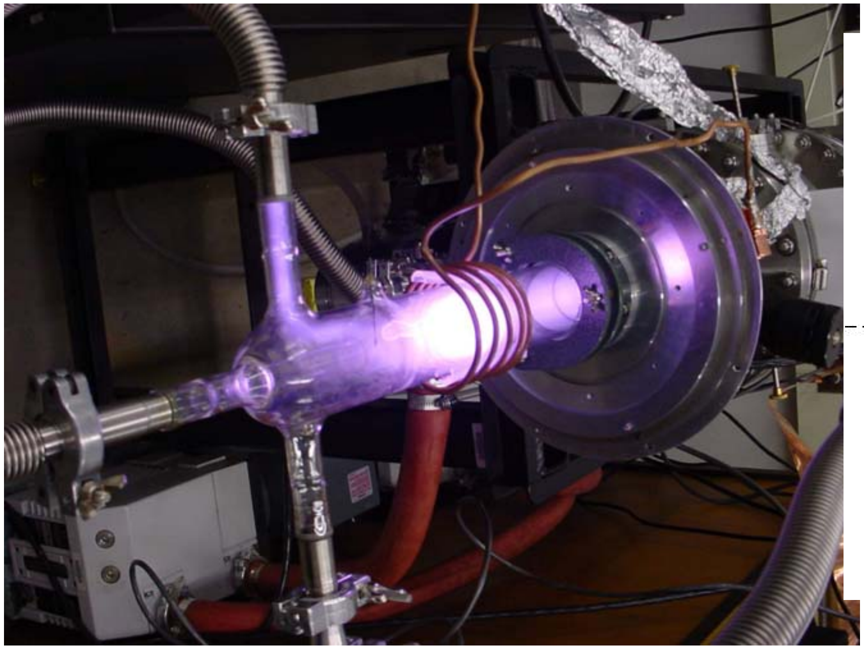


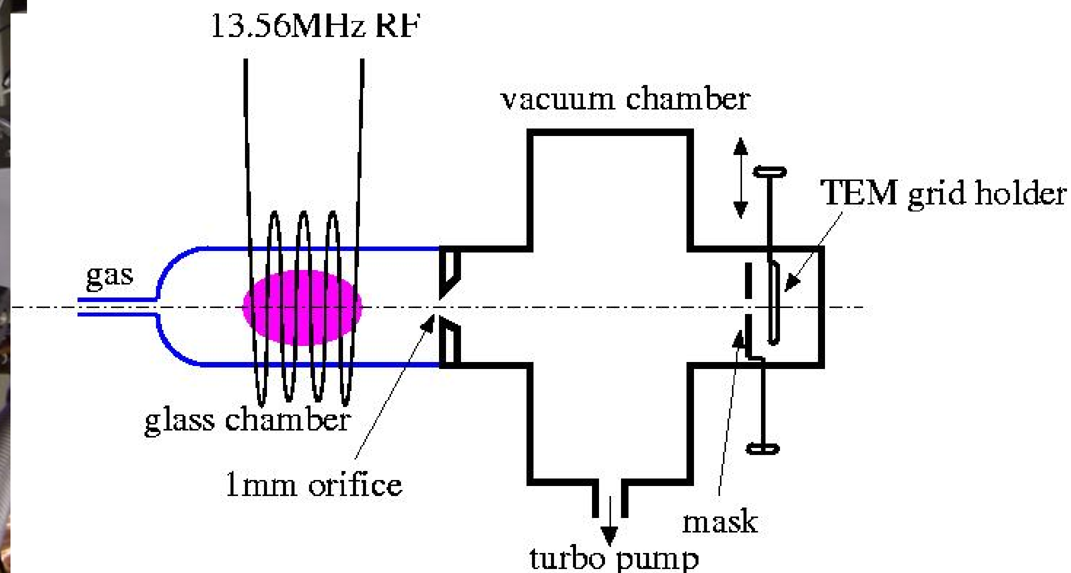


courtesy of Z. Shen, S. Campbell

Simulation of Schottky Barrier Transistor. Left: Charge density for 50 nm particle under V_{DS}=V_{GS}=1 V. Right: Family of curves.

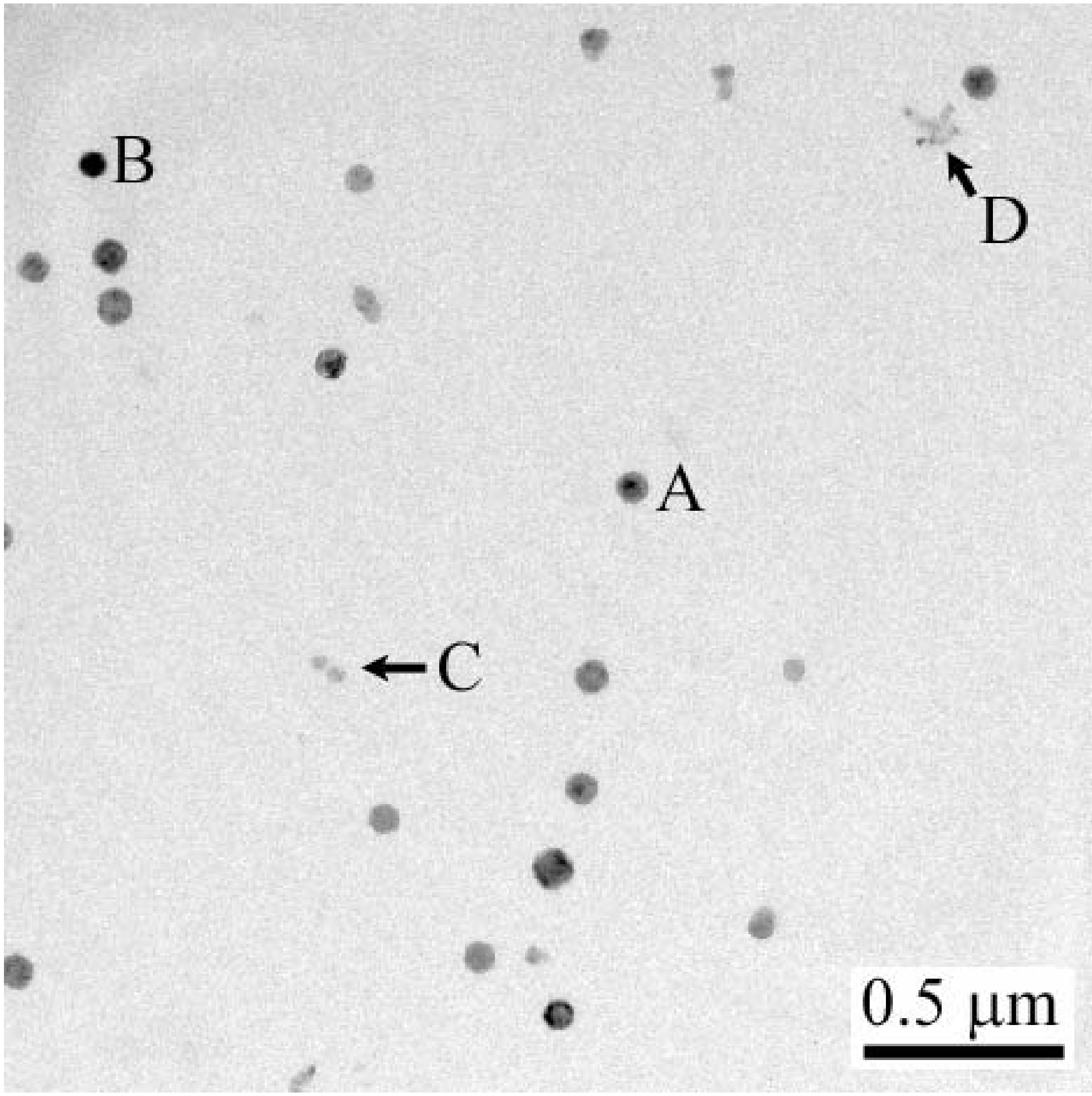
Nanoparticles in inductive plasmas





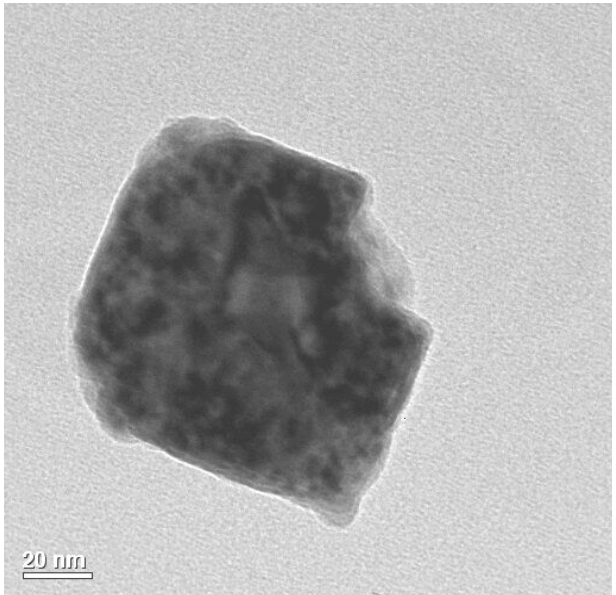
gas mixture:	SiH_4:He:Ar (typ.: 1:19:80)
total gas flow:	3-4 sccm
total pas pressure:	500-700 mTorr
SiH_4 part. pres.:	2-7 mTorr
RF power:	120-150 W
plasma volume:	100 cm^3

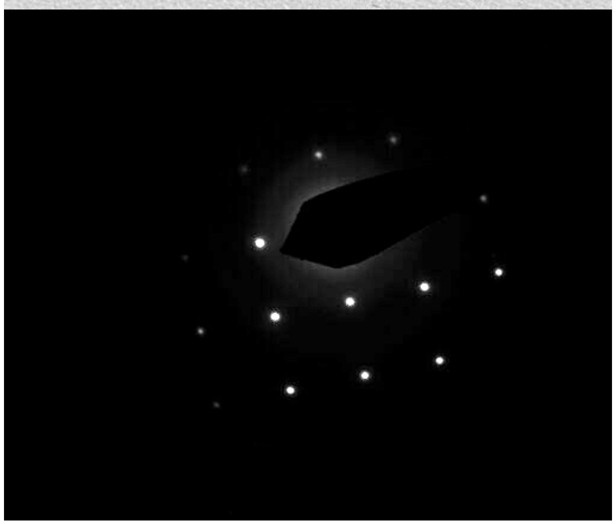
Nanoparticles in inductive plasma



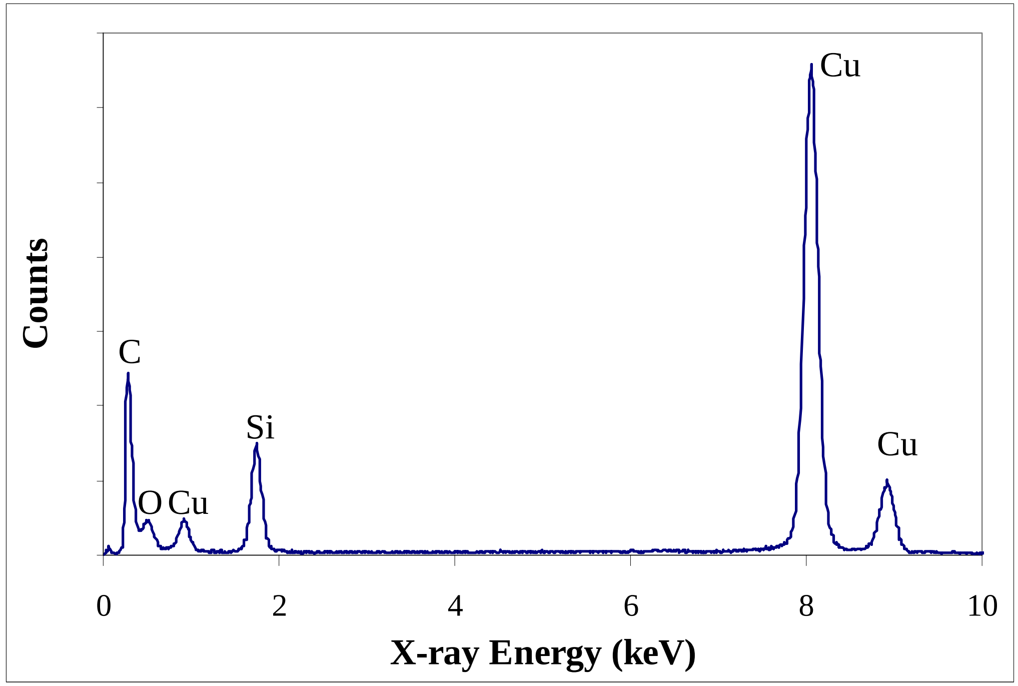
courtesy of C. Perrey, C. B. Carter

Nanoparticles in inductive plasma



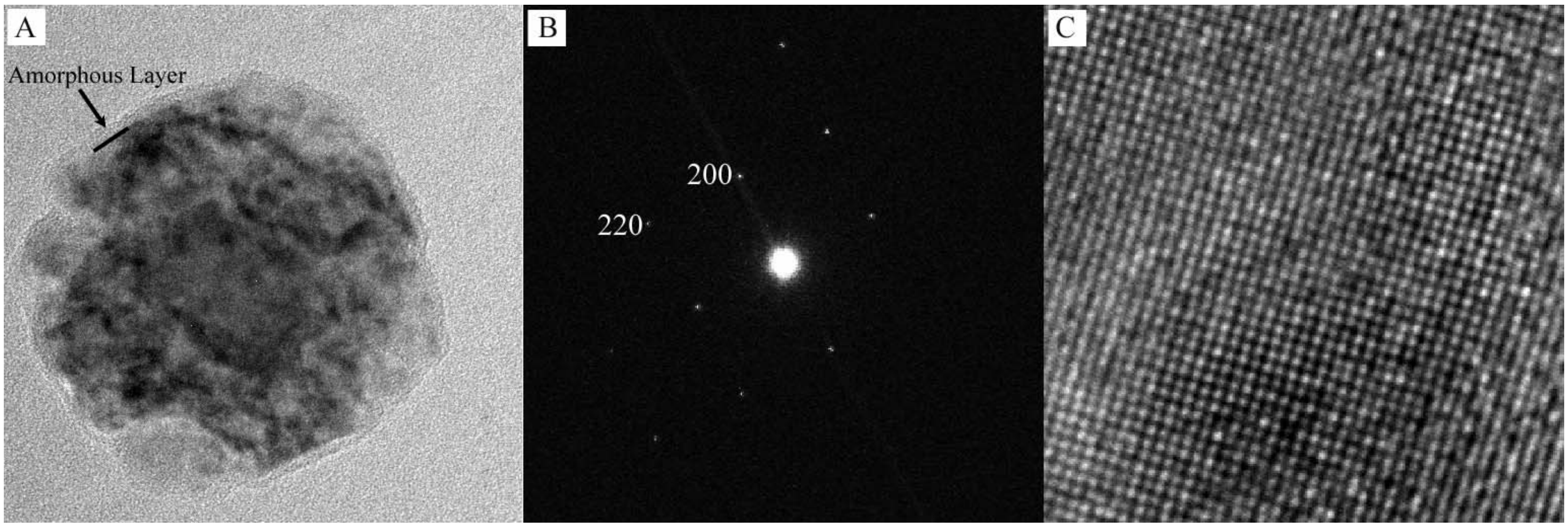


courtesy of C. Perrey, C. B. Carter



Particles are Single-Crystal Si, possibly with oxide layer.

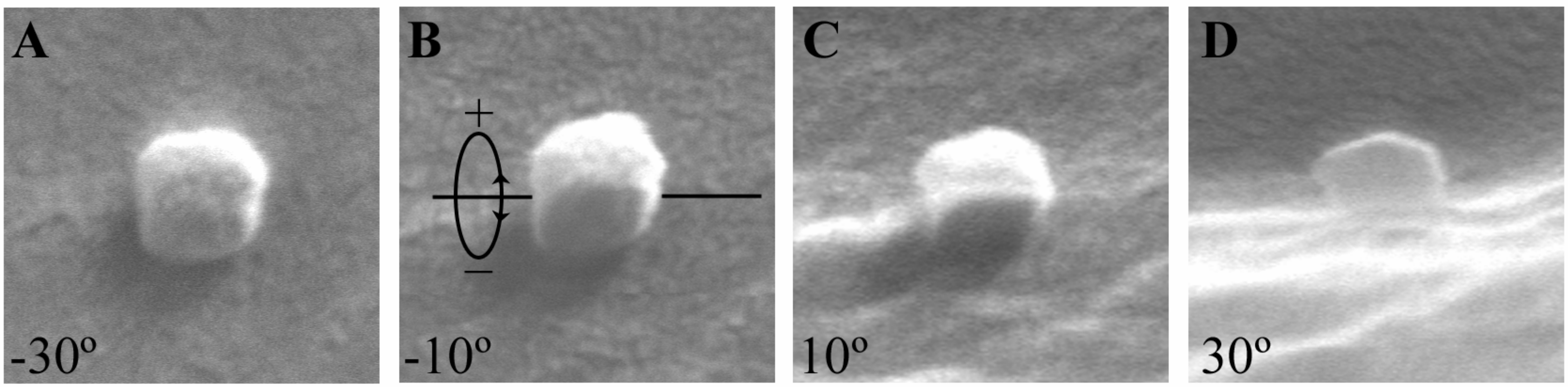
Single-Crystal Nanoparticle



courtesy of C. Perrey, C. B. Carter

"Cubic" nanoparticle showing [001] diffraction pattern of diamond-cubic Si.

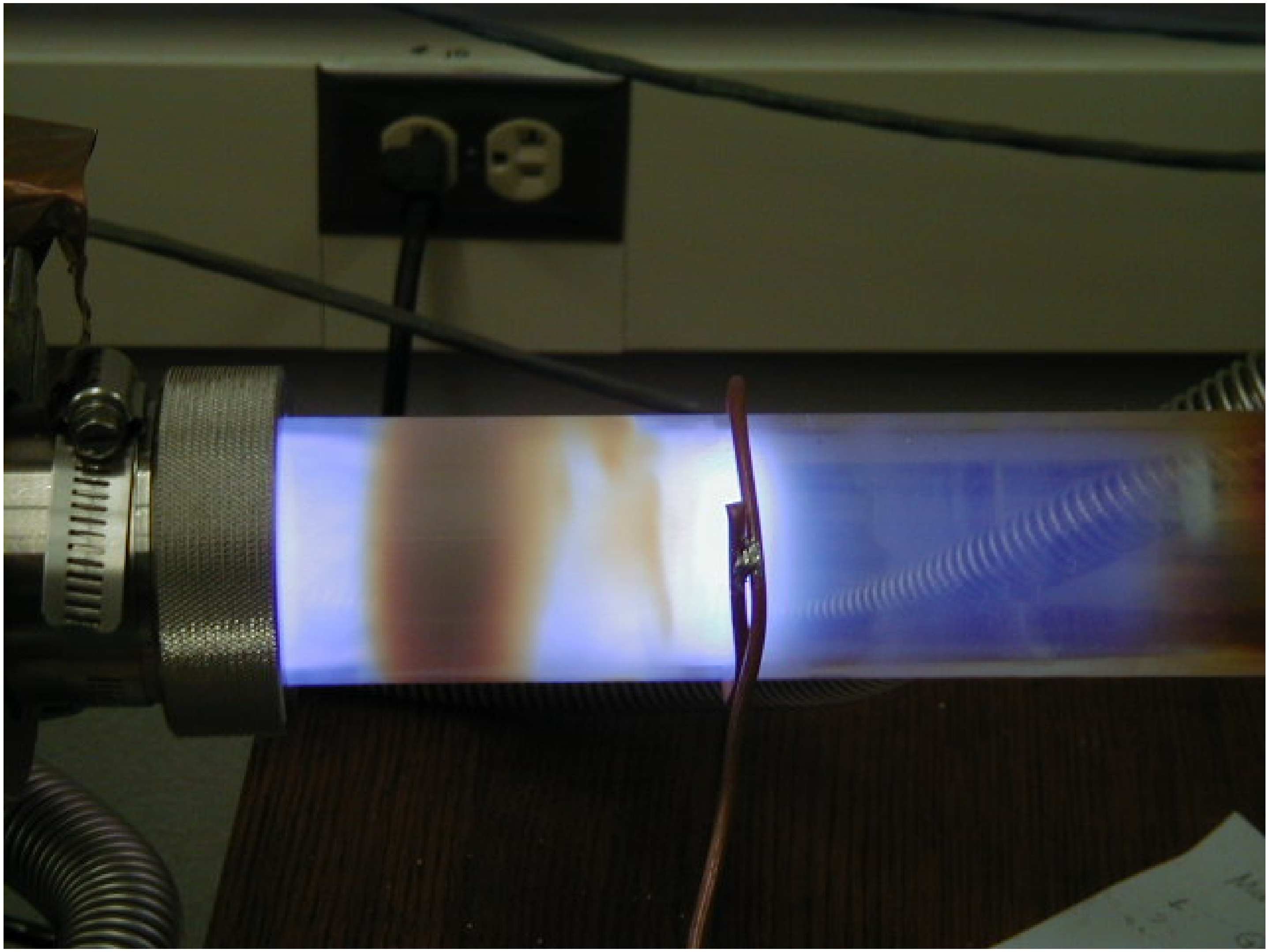
Single-Crystal Nanoparticle



courtesy of C. Perrey, C. B. Carter

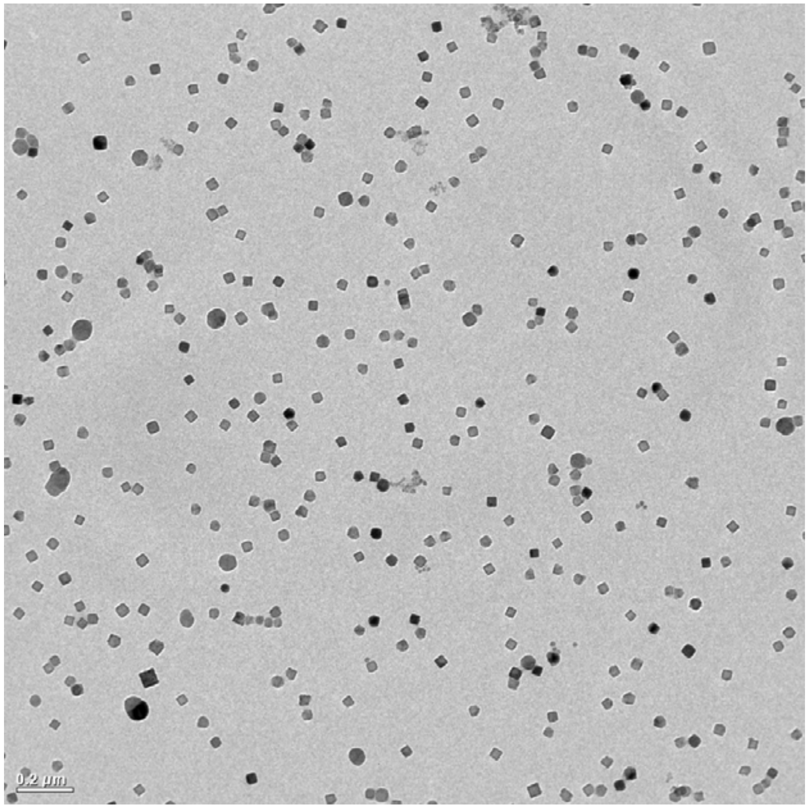
SEM of Si Nanoparticle

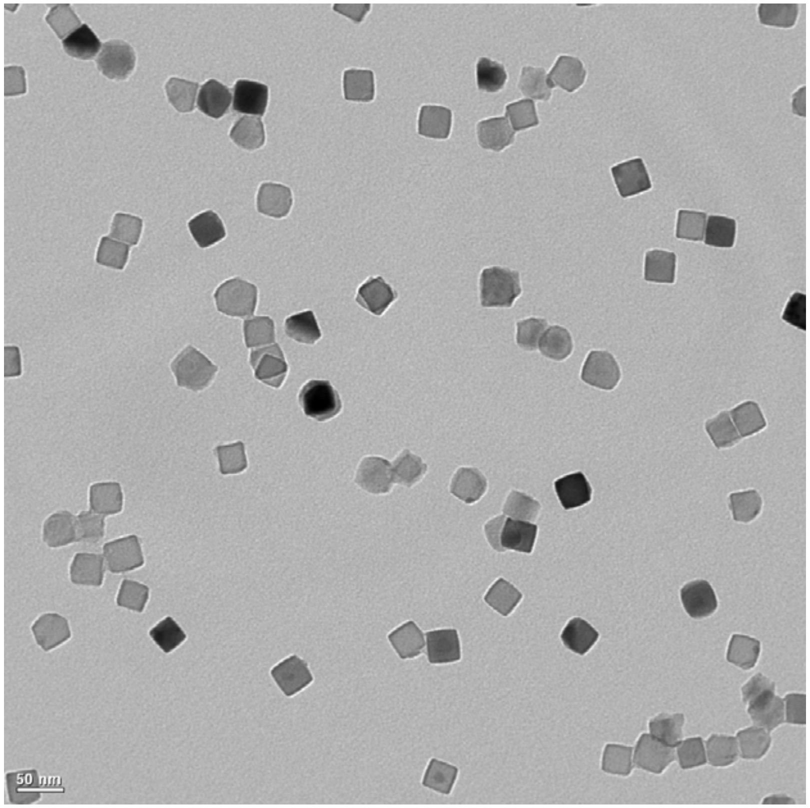
Single-Crystal Nanoparticle



Unstable “Capacitive” Discharge Mode

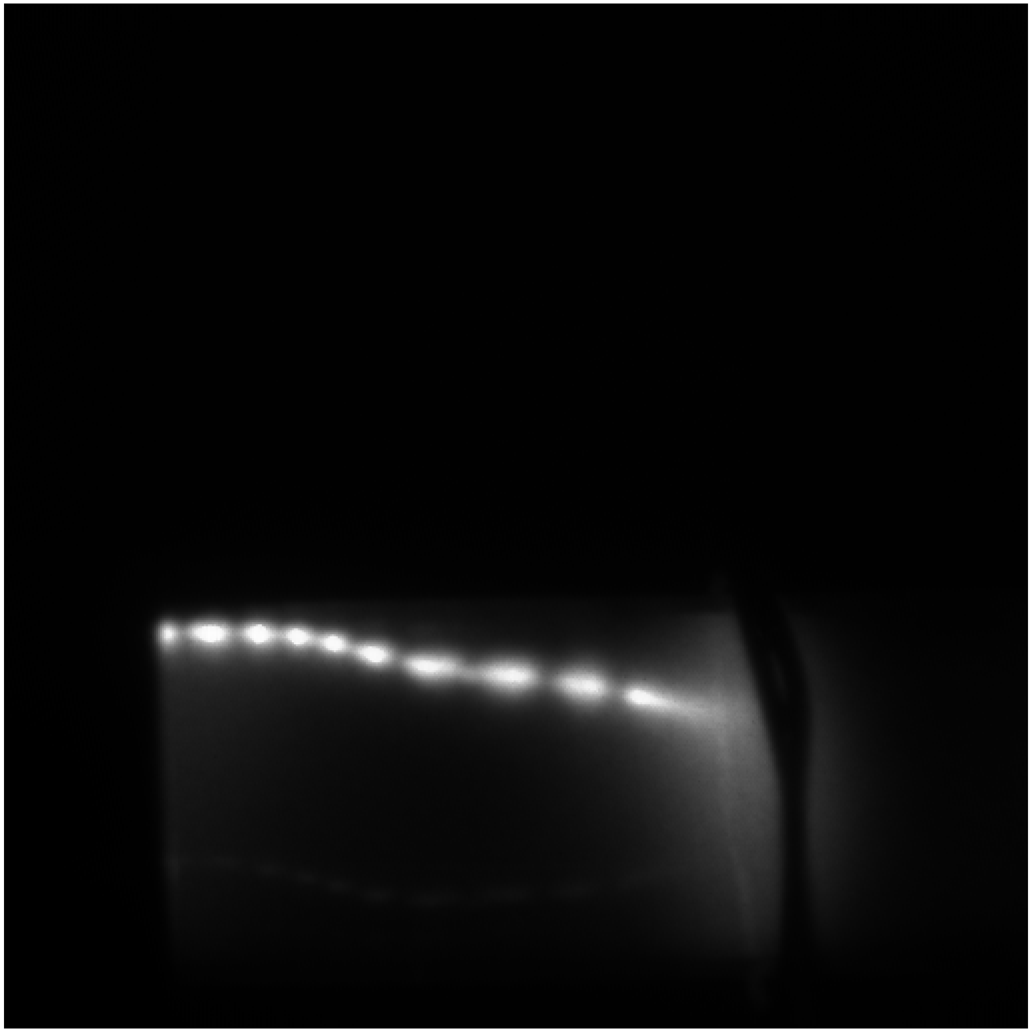
Single-Crystal Nanoparticle





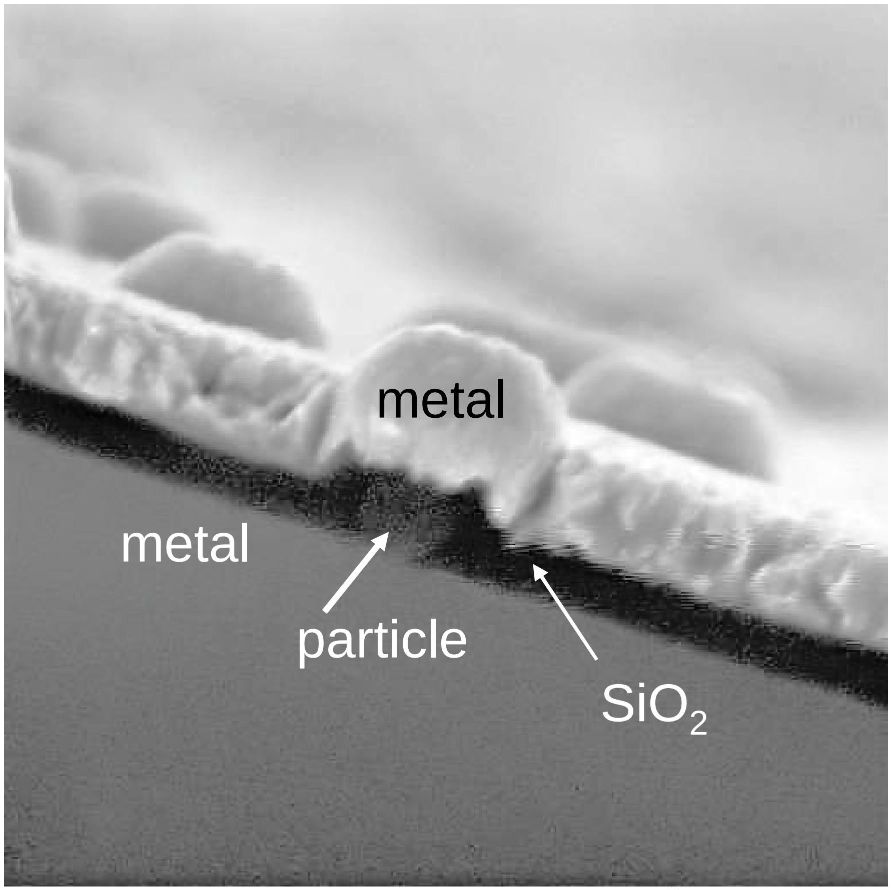
Partciles from Unstable “Capacitive” Discharge Mode

Single-Crystal Nanoparticle

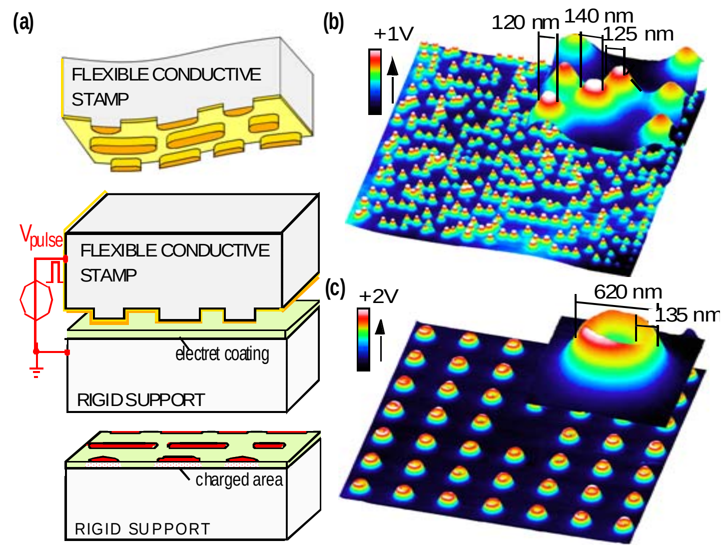


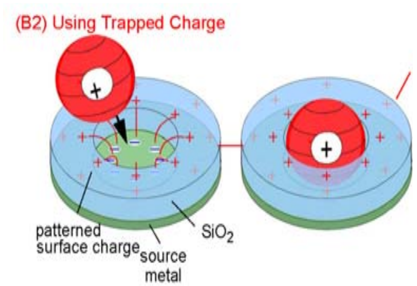
High-Speed ICCD movie

Science Fiction??



courtesy of Z. Shen, S. Campbell 200nm 100000X





Electrical contact to amorphous nanoparticles.

Work of Heiko Jacobs' group.

What is next?

- Optimize plasma process: produce monodisperse particles.
- Study electrical properties ⇔ Campbell group.
- Understand if particles are extracted with remaining charge ⇔ Jacobs Group.
- Can charge be used for electrostatic manipulation? Focusing, deflection?

Demonstrate Nanoparticle Devices ⇔ Cambell, Carter, Jacobs groups

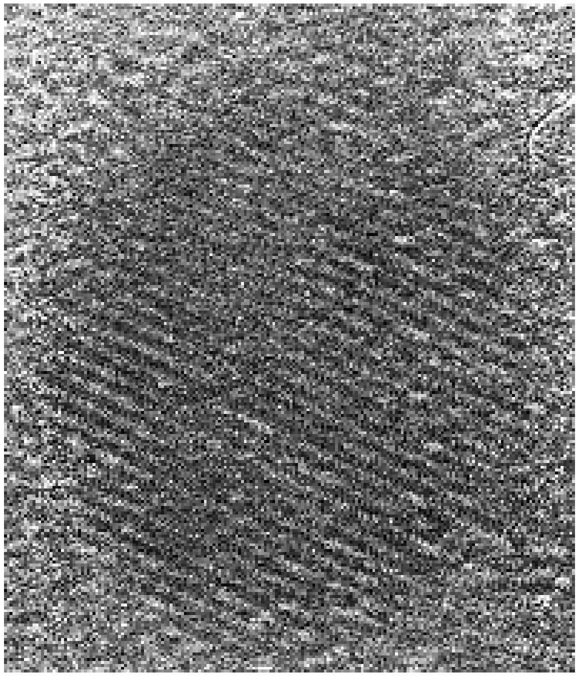
Nanostructured Si-films

S. Thompson[1], C. Perrey[2], J. Belich[3],
C. B. Carter[2], J. Kakalios[3], U. Kortshagen[1]

[1]Mechanical Engineering
[2]Chemical Engineering and Materials Sci.
[3]Physics

Nanostructured Si Thin Films

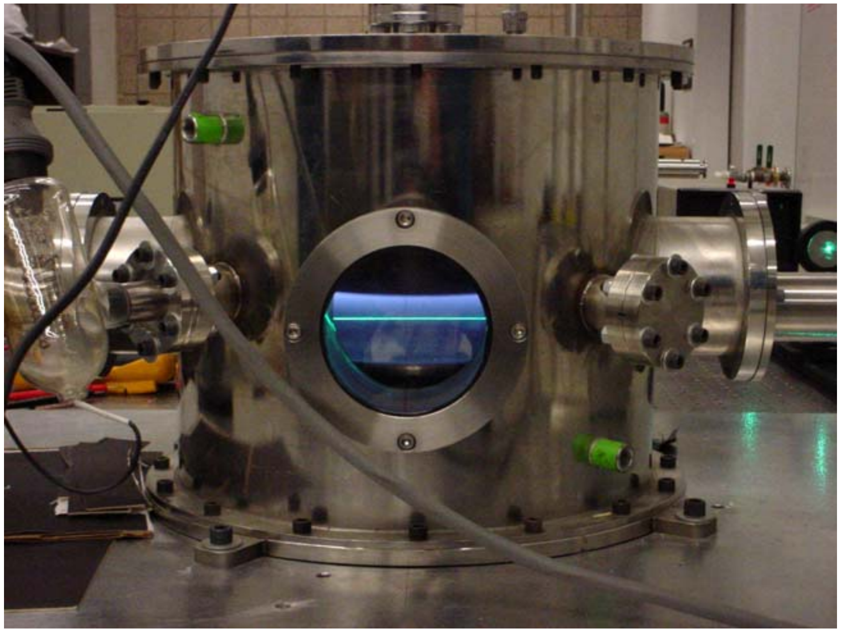
- Dispersed nanocrystallites in an “amorphous” matrix
- Compared to a-Si:H
  - Similar optical properties
  - Improved transport properties
  - Enhanced medium range order
  - Reduced Staebler-Wronski effect

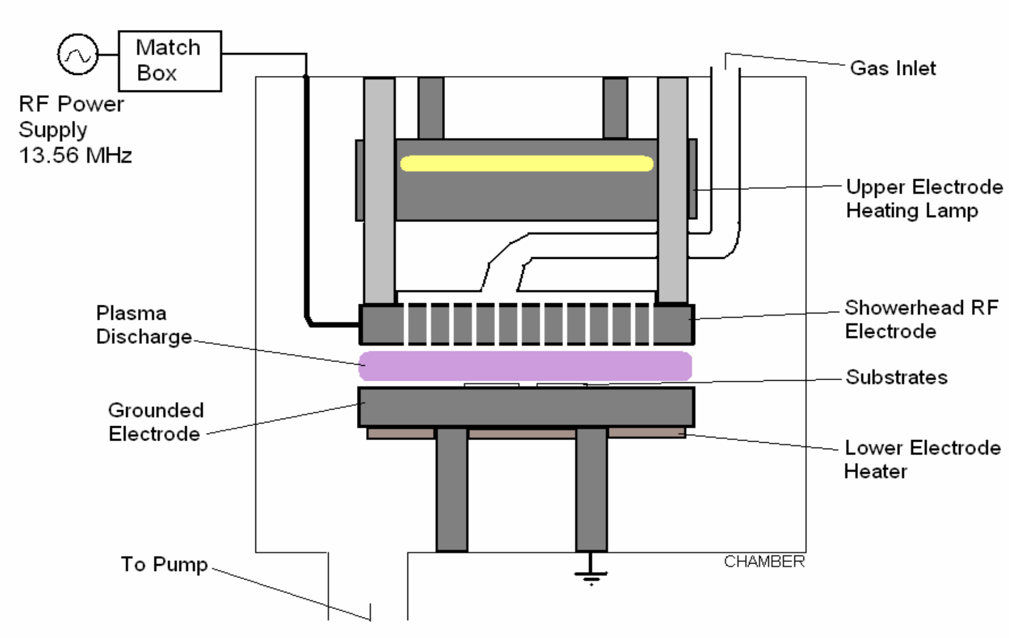


HRTEM image of a 4 nm nanocrystalline inclusion.

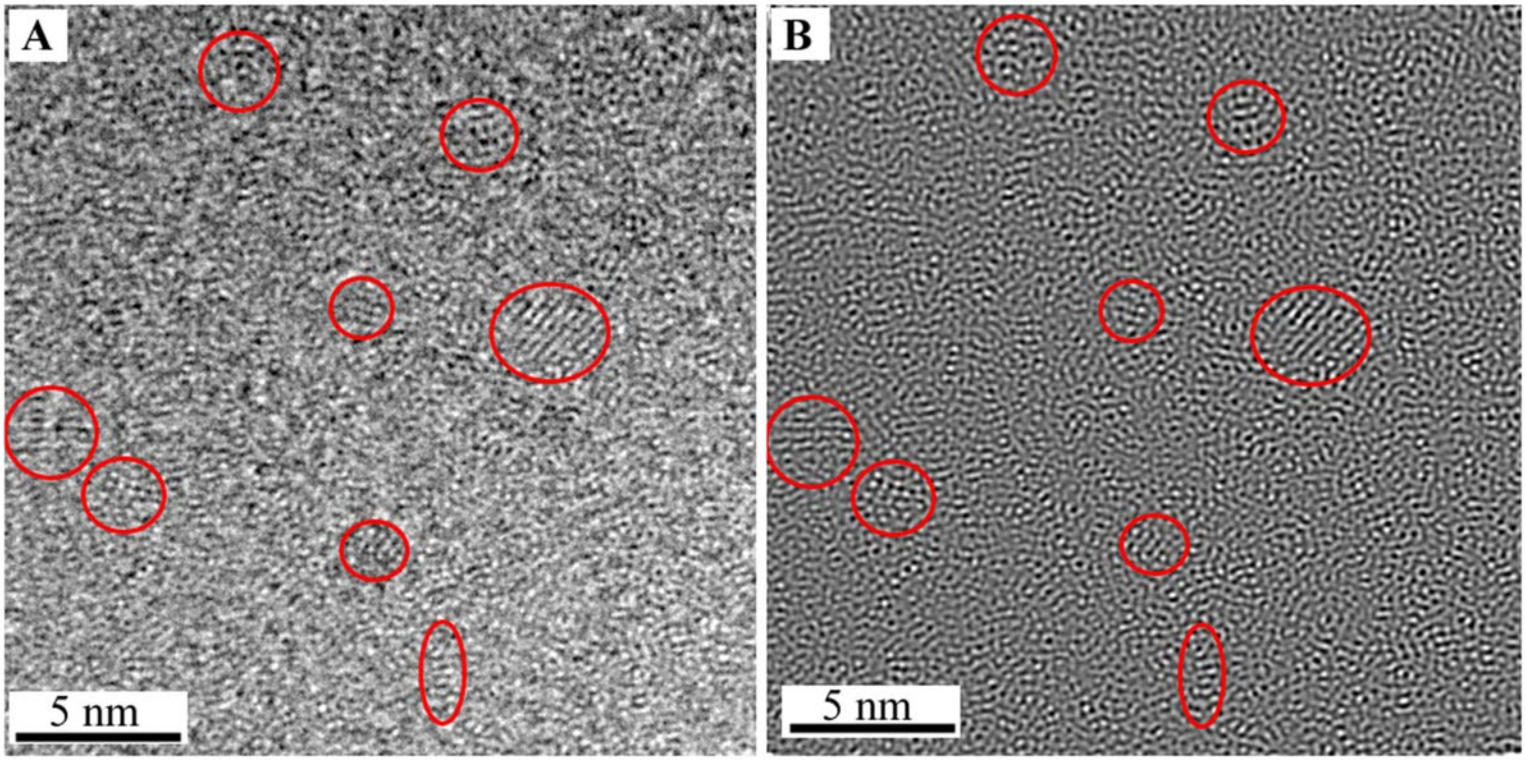
C. Longeaud, J. Kleider, P.R. Cabarrocas et al./ J. Non Cryst. Solids. 277-230 (1998) 96-99.

Set-up for ns-Si Film Growth





ns-Si films

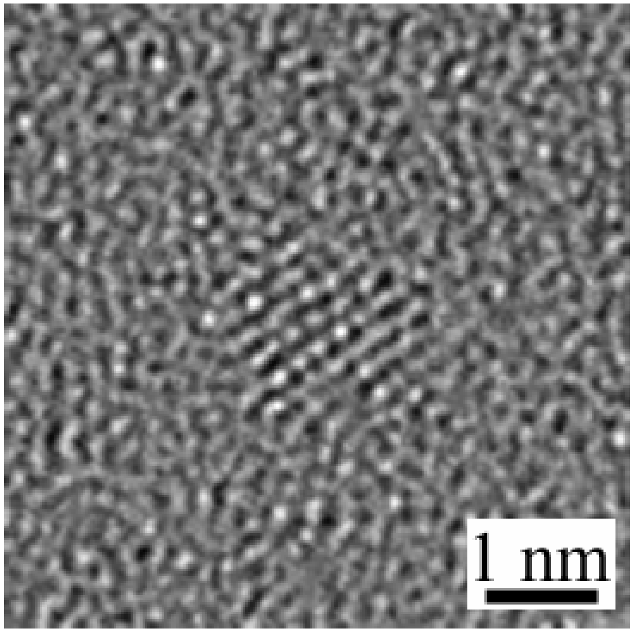


ns-Si:H film deposited at 1450 mTorr.

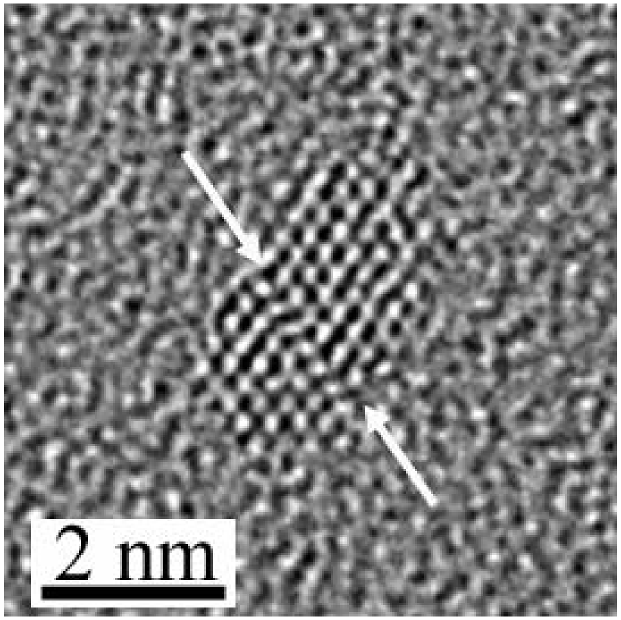
Film Structure

ns-Si:H

1450 mTorr



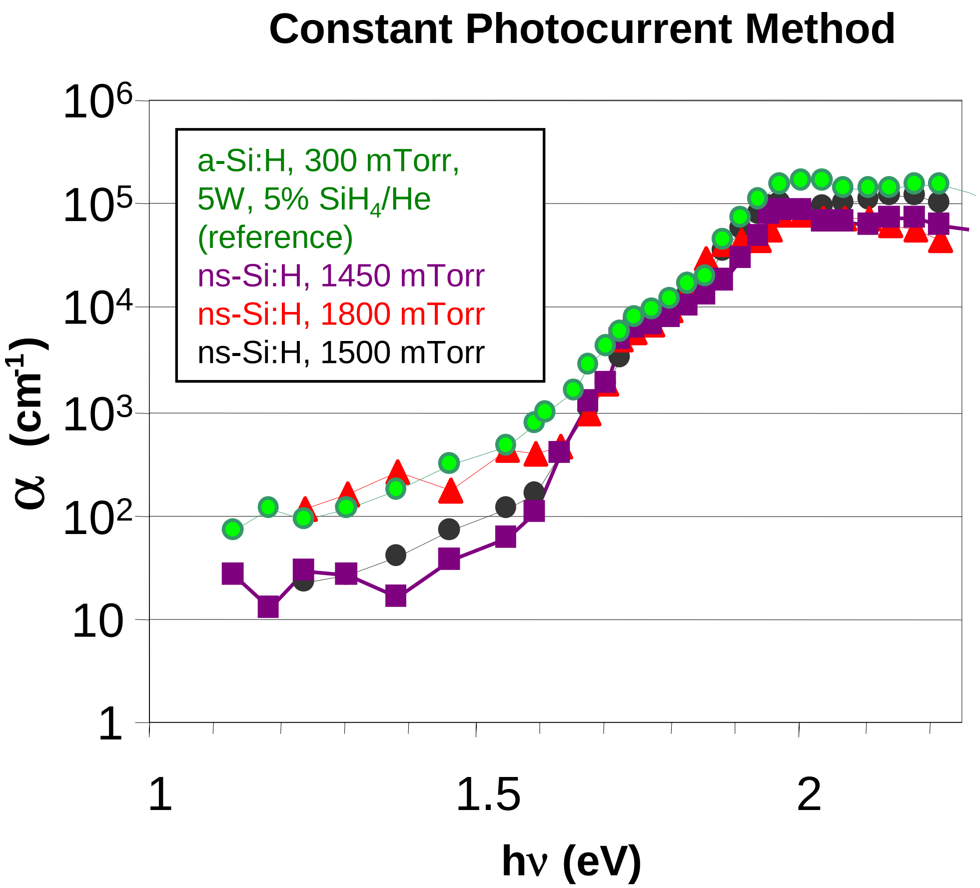
~1.5 nm Si particle

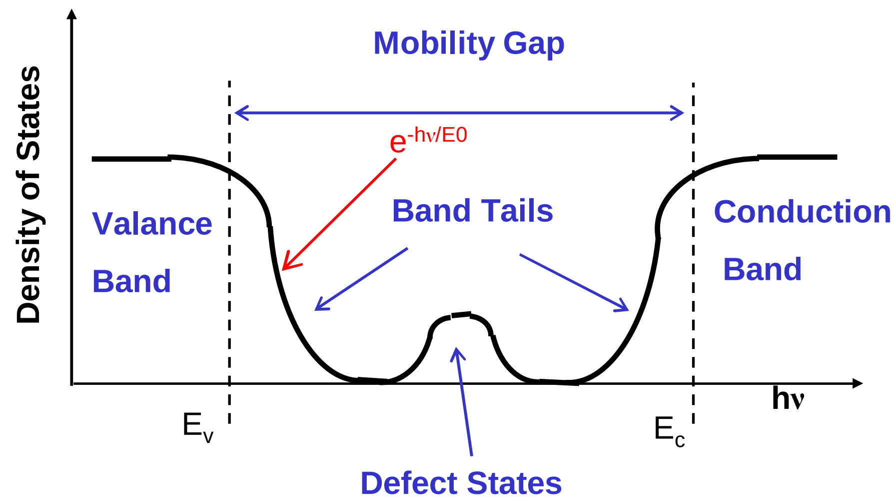


Si nanoparticle with a stacking fault

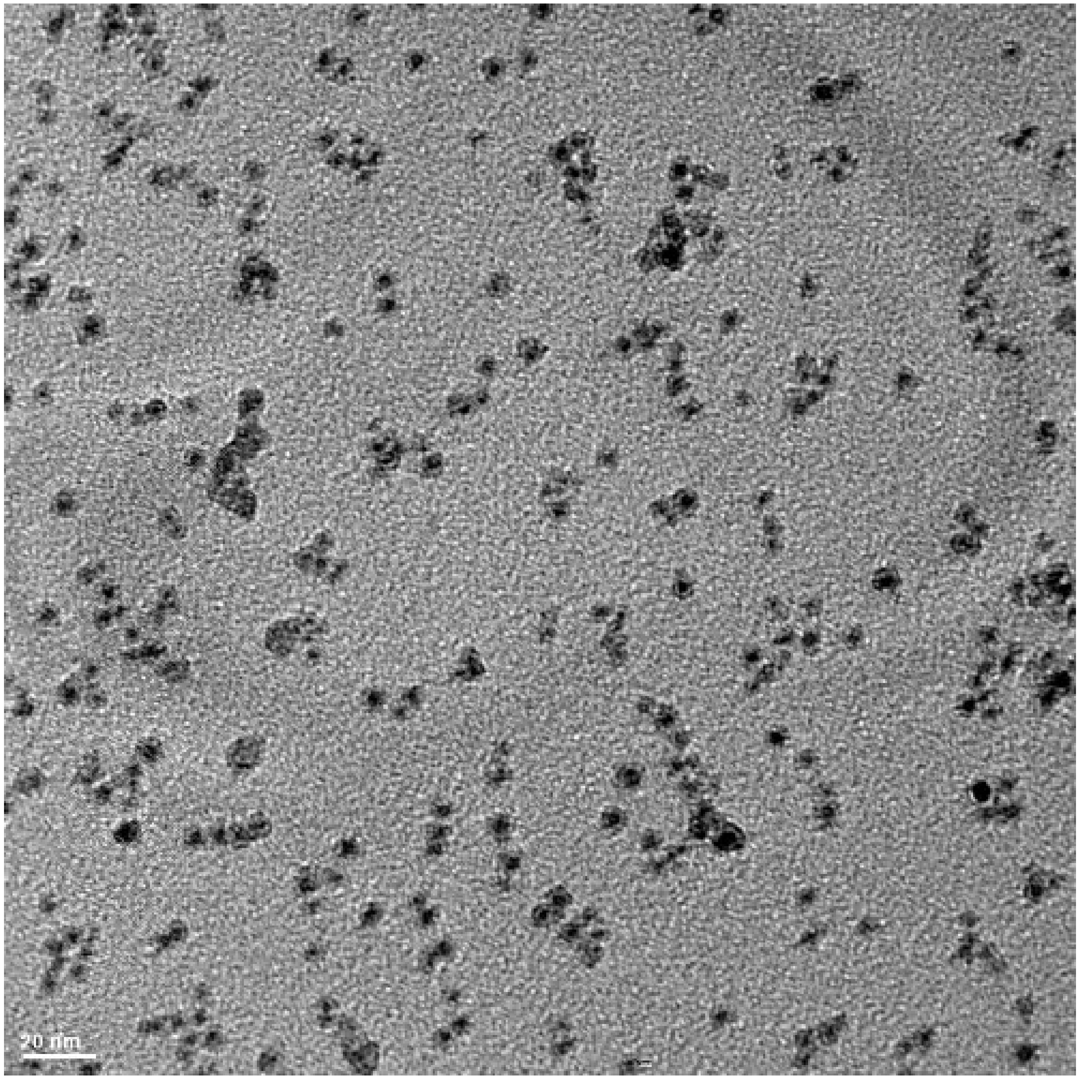
Images taken with a Philips CM 200 FEG with a spherical aberration corrector. Courtesy of C. Perrey and C. Barry Carter (Dept. of Chemical Engr. & Material Sci) with Dr. Markus Lentzen and Prof. Knut Urban (Research Center Jülich, Germany).

Optical Absorption Measurements





Free-standing silicon particles



Conclusions and Future Work

- ns-Si:H films produced with 2-3 nm crystals in film
- ns-Si:H show lower defect density than a-Si:H films.

Future Work:

- Role of particles in film?
- Co-deposition of particles of material A into films of material B.

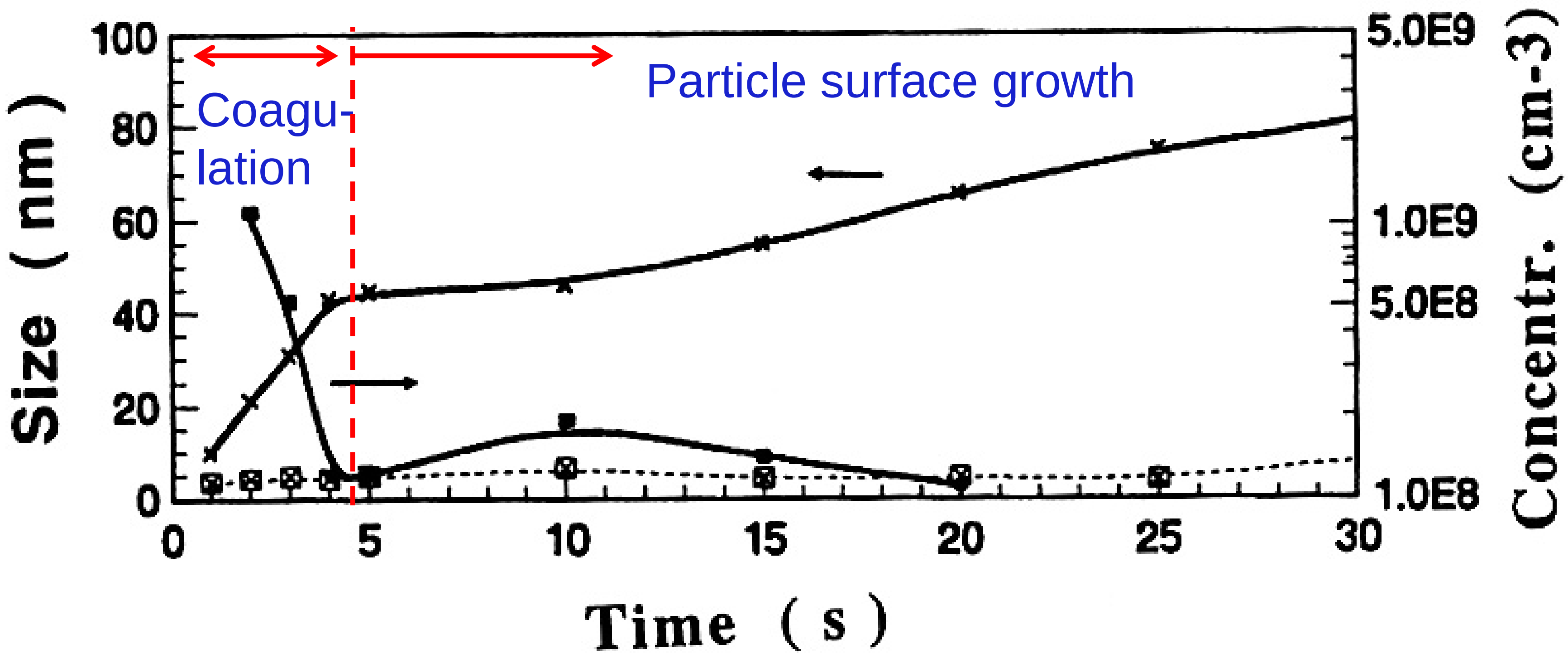
Particle Growth Modeling

U. Bhandarkar, S. Warthesen,
S. Girshick, U. Kortshagen

Mechanical Engineering

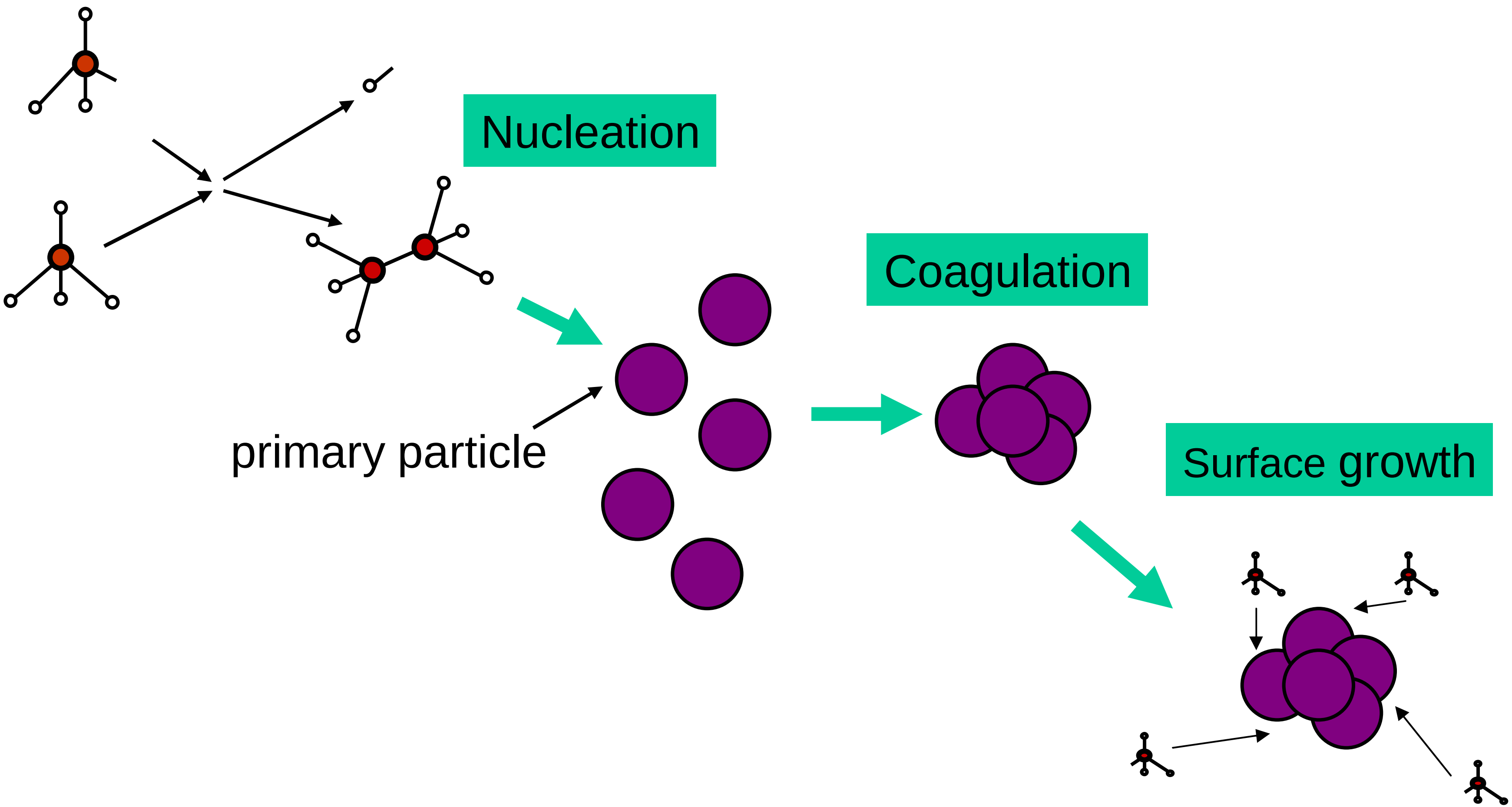
Particle Growth Scenario

3.8% SiH_4 in Ar, 117 mTorr

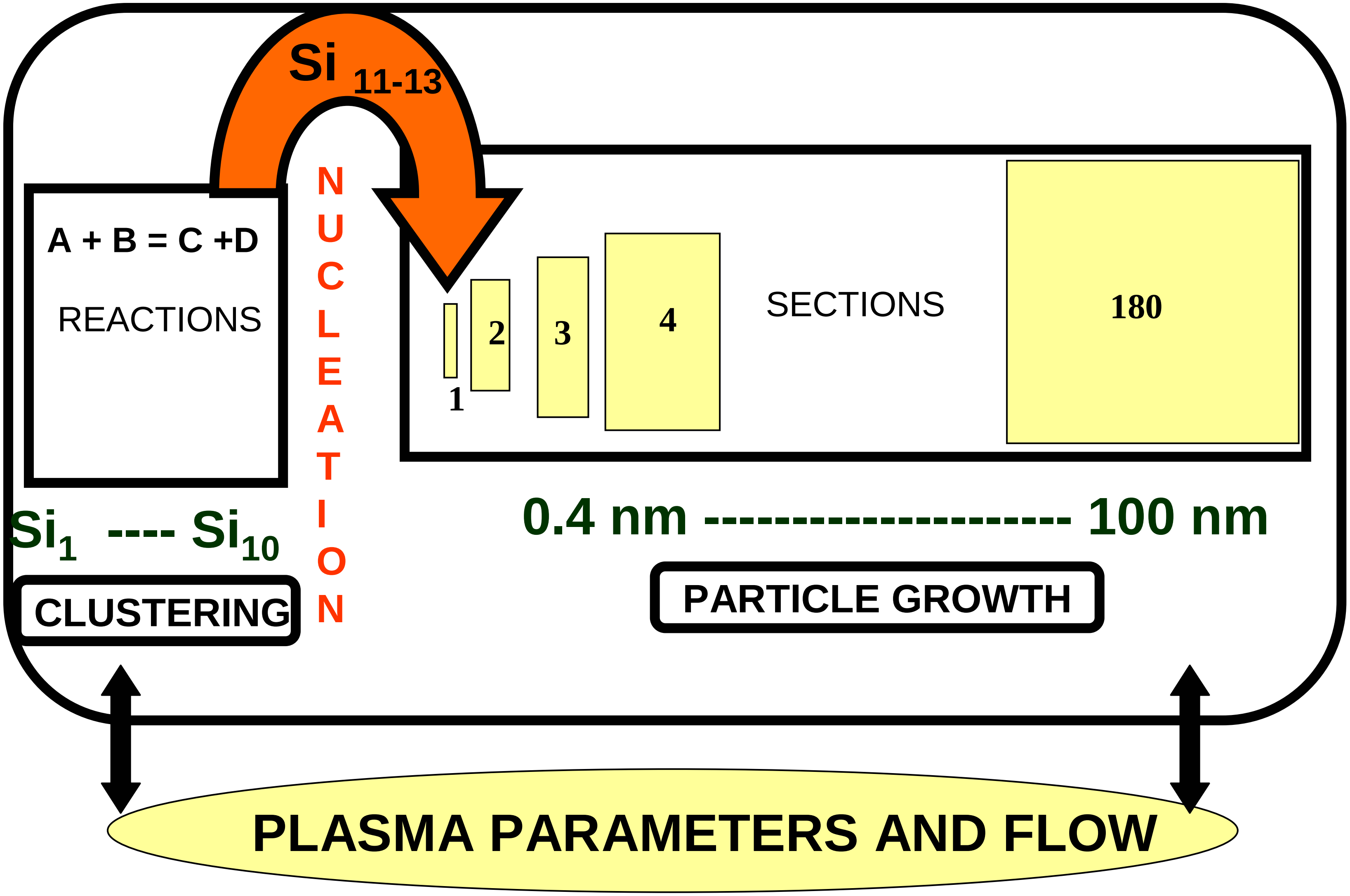


Boufendi & Bouchoule, *Plasma Sources Sci. Technol.* **3**, 262 (1994)

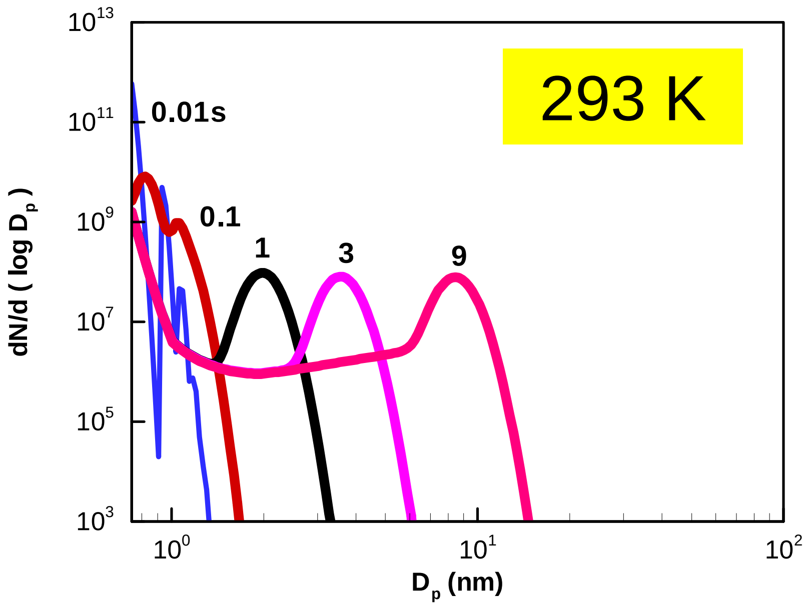
Particle Growth in Plasmas

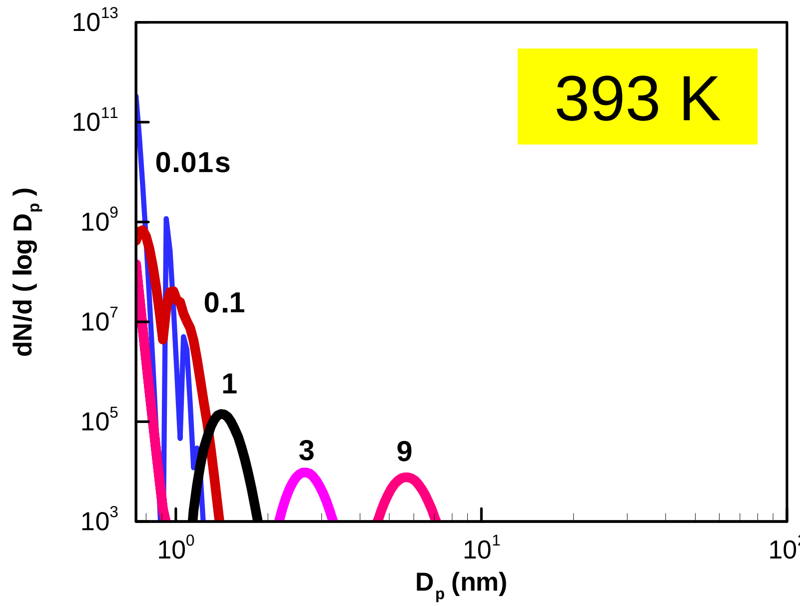


Overview over Growth Model



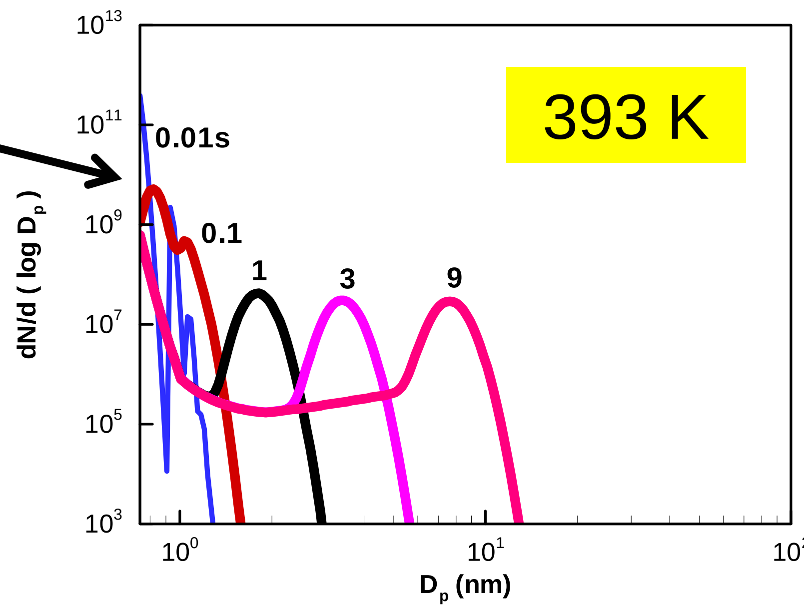
Effect of Gas Temperature





all reactions at 393K

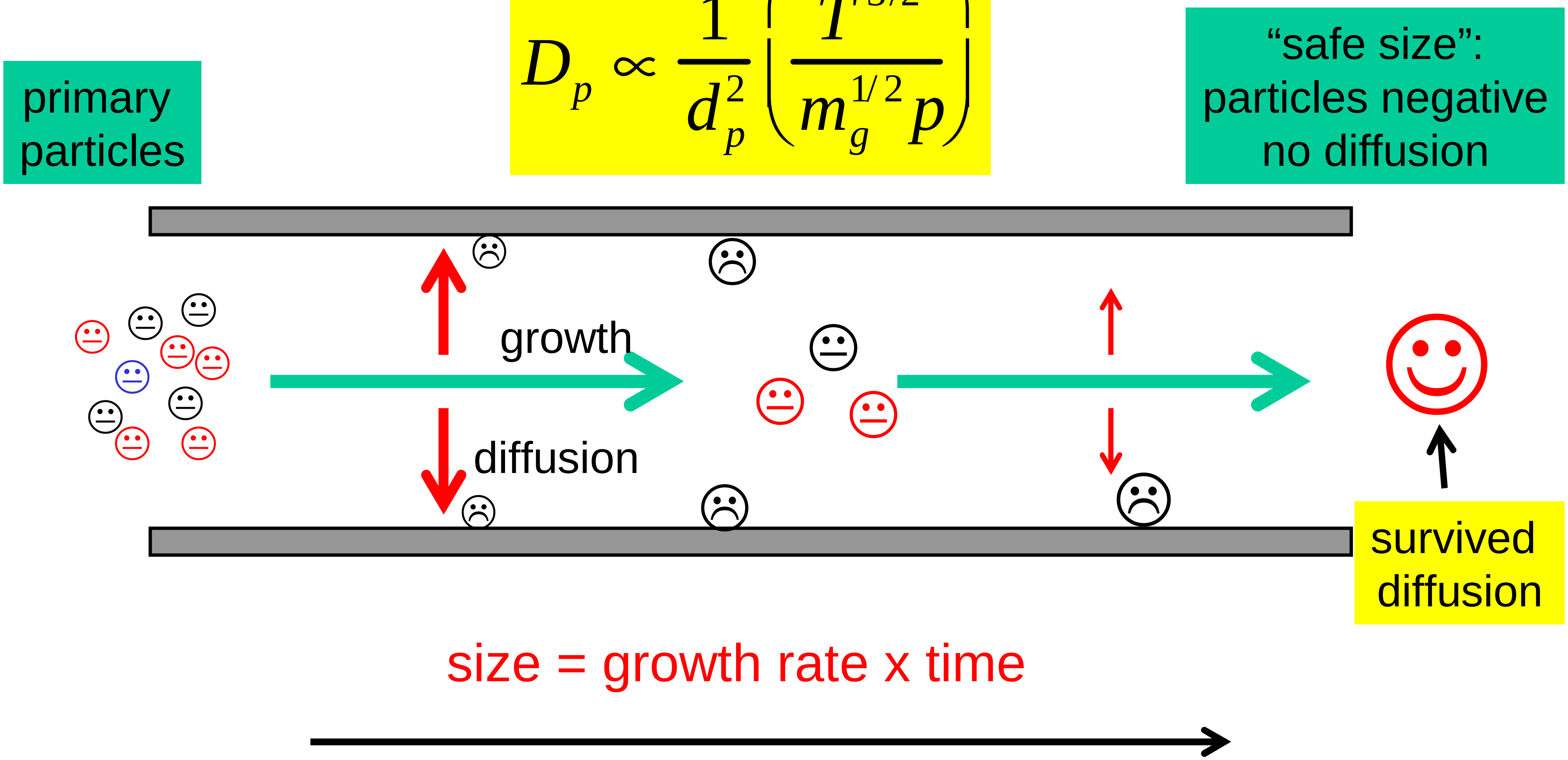
only diffusion at 293K



3.8% SiH_4 in Ar, 117 mTorr

Growth and Diffusion

$$D_p \propto \frac{1}{d_p^2}\left(\frac{T^{3/2}}{m_g^{1/2}\,p}\right)$$

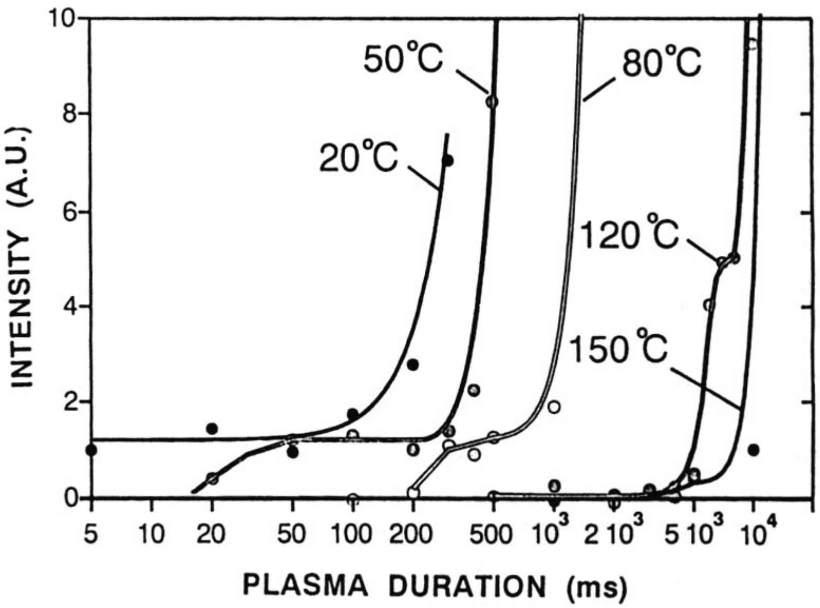


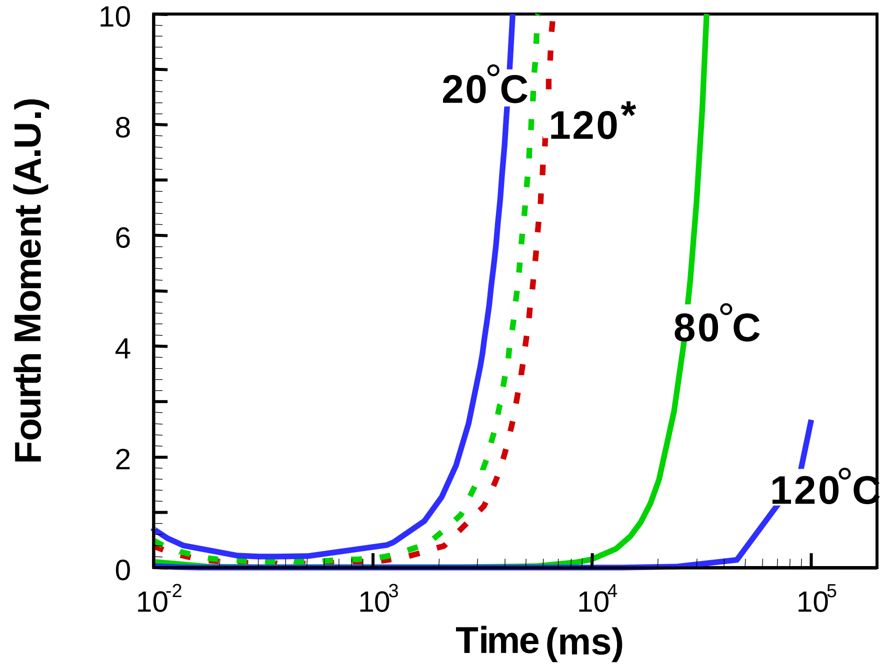
Effect of Gas Temperature

3.8% SiH_4 in Ar, 117 mTorr

LIPEE measurement

$\propto N_p d_p^4$





Temperature dependence of growth rate and diffusion explains this effect.

Conclusion

Important Results of Model:

- Positive ion density is threshold density for coagulation.
- Anions are important for fast clustering reactions.
- Temperature dependence of diffusion explains retarded nucleation.