Nanoparticle Synthesis and Assembly from Atomistic Simulation Studies

By Takumi Hawa

School of Aerospace & Mechanical Engineering

The UNIVERSITY of OKLAHOMA

Oklahoma Supercomputing Symposium 2008
October 7
Supported by NSF, ARL, & NIST
Why Nanoparticle

Some 75% of chemical manufacturing processes involve fine particles at some point.

- tires & toners
- food
- personal care & cosmetics
- pharmaceuticals
- waste

Proper manufacturing processes:
- improve cost
- minimize waste
- improve quality
- provide safety

Design & handling of these fine particles makes the difference between success & failure.
Particle Synthesis

- **Liquid Phase**
  - Easier to control size
  - Production rate is low

- **Vapor Phase**
  - High production rate
  - Inexpensive!
  - Difficult to control size

Challenge: Control size in vapor phase!
Vapor phase synthesis of nanoparticles

- Chemical precursor vapor + carrier gas
- Nucleation of monomer via chemical or physical gas to particle conversion
- Rapid particle growth via coagulation
- Particle number decreases
- Early stage of very-fine aggregate formation
Collision & Sintering Time

\[ t_{\text{sintering}} \]

\[ t_{\text{collision}} \]

Zachariah et al (1996)

Zachariah et al (1996)
Vapor phase synthesis of nanoparticles

Particle growth and morphology are determined by the competition of collisions and sintering.
Hydrogen Passivation Surface

- Reactivity?
- Property?
- Sintering?

$t_{\text{collision}} \& t_{\text{sintering}}$
Contents

- Size of nanoparticles
- Shape of nanoparticles
- Assembly of nanoparticles.
SIZE
CONTROL
Collision of H coated particles (liquid & solid) (cross-section view)

- 6 nm particles at 600 & 1500 K
Johnson et al. (1971) suggested

\[ \pi a_0^2 \sim N^{4/9} \text{atoms} \]

\[ \frac{3}{2} kT = \frac{1}{2} mv^2 \]

\[ KE_{app} = \frac{1}{3} \frac{mv^2}{k} \]
Reactivity of the Coated Particles

Critical approach energy for reaction

\[ \frac{3}{2} kT = \frac{1}{2} mv^2 \]

\[ KE_{app} = \frac{1}{3} \frac{mv^2}{k} \]

- size \( \uparrow \), harder to react
- \( T \uparrow \), easier to react
- No thermal reaction
  - \( t_{col} \rightarrow \infty \)

\( \text{Phys. Rev. B 69, 35417 (2004)} \)
Mathematical Model

Assumption

1) Viscous fluid
2) Maintain a spherical shape
   (made by Frenkel (1945))

Continuity

\[ \Delta S = 4\pi a^2 \left[ \Delta \theta (-\sin \theta) + O(\Delta \theta^2) \right] \]

Energy balance

\[
\frac{16}{3} \pi a^3 \eta \gamma^2 = 4\pi a^2 \sigma \gamma
\]

\[ \sigma = \text{surface tension} \]
\[ \eta = \text{viscosity} \]
\[ \gamma = \text{velocity gradient} \]

Effective passivation surface area

\[ \xi = \frac{\text{Passivated surface}}{\text{Effective contact area}} = \frac{\pi a f_c}{\pi \left( a f_c + a^2 \sin^2 \theta \right)} \]

- \( \xi = 1 \) (initially)
- Most of the energy is consumed by relocation of the surface atoms
- \( \xi = 0 \) towards the end

*Phys. Rev. B 71, 165434 (2005)*
Mathematical Model

Solving the energy equation gives

\[ \beta = 0 \text{ (bare)} \]
\[ \beta > 0 \text{ (coated)} \]

Mathematical Model

\[ t = \frac{2}{3} \eta d \int_{0}^{\pi/2} \frac{\sin \theta}{\sigma - \beta \xi'(\theta)} \, d\theta \]

\[ t_{\text{Frenkel}} = \frac{2\eta d}{3\sigma} \]

by Frenkel (1945)

\[ d = \text{diameter} = 2a \]

Sintering (Bare vs. Coated)

cross-section view

- 6 nm droplets at 1500 K
- KE_{app} = 110,000 K
Dynamics of Sintering

\[ t = \frac{2}{3} \eta d \int_0^{\pi/2} \frac{\sin \theta}{\sigma - \beta \xi(\theta)} \, d\theta \]

\[ \eta = 5.9 \text{ centipose} \]
\[ \sigma = 0.83 \text{ J/m}^2 \]

6 nm particles at 1500K

- \( (\sigma - \beta)/\sigma = 3.25 \times 10^{-6} \)

Work done by relocation of surface atoms dominates the initial process

- \( \sigma_{\text{coated}}/\sigma_{\text{bare}} = 0.54 \)

\( \text{Mb/Mc} = 0.48 \)

After the initial process, the surface tension dominates the sintering process

40 particle chain aggregate

- $T = 1500\, \text{K}$
- $2.5\, \text{nm primary particles}$
Sintering Time for a Chain Aggregate

Universal relationship that only depends on chain length.

\[ t/d = \frac{\eta \left( \frac{1}{2} \right)^{\frac{1}{3}}}{\sigma} (A + B + C) \]

\[ A = -2\sqrt{3} \left\{ \text{Atan} \left( \frac{1 - 2^{\frac{1}{3}}}{\sqrt{3}} \right) - \text{Atan} \left( \frac{1 - 2\left(\frac{\pi}{V}\right)^{\frac{1}{3}}}{\sqrt{3}} \sqrt{L_0} \right) \right\} \]

\[ B = -2 \left\{ \ln \left[ 1 + 2^{\frac{1}{3}} ight] - \ln \left[ 1 + \left( \frac{\pi}{V} \right)^{\frac{1}{3}} \sqrt{L_0} \right] \right\} \]

\[ C = \ln \left[ 1 - 2^{\frac{1}{3}} + 2^{\frac{2}{3}} \right] - \ln \left[ \left( \frac{\pi}{V} \right)^{\frac{1}{3}} \sqrt{L_0} + \left( \frac{2\pi}{V} \right)^{\frac{2}{3}} L_0 \right] \]

\[
\begin{align*}
\times & \quad \text{500 atoms/particle (MD)} \\
\bigtriangleup & \quad \text{1000 atoms/particle (MD)} \\
\lozenge & \quad \text{2000 atoms/particle (MD)} \\
\bigcirc & \quad \text{4000 atoms/particle (MD)} \\
\end{align*}
\]

- Independent of primary particle diameter.

Excellent agreement with MD.

Sintering Time for a Chain Aggregate

\[
t/d = \frac{\eta \left( \frac{1}{2} \right)^{\frac{1}{3}}}{\sigma} (A + B + C)
\]

\[
A = -2\sqrt{3} \left[ \text{Atan} \left( \frac{1 - 2^{2/3}}{\sqrt{3}} \right) - \text{Atan} \left( \frac{1 - 2\left(2\sqrt{\pi/V}\right)^{2/3}}{\sqrt{3}} \sqrt{L_0} \right) \right],
\]

\[
B = -2 \left[ \ln \left( 1 + 2^{2/3} \right) - \ln \left( 1 + \left( 2\sqrt{\pi/V} \right)^{2/3} \sqrt{L_0} \right) \right], \text{ and}
\]

\[
C = \ln \left( 1 - 2^{2/3} + 2^{4/3} \right) - \ln \left( 1 - \left( 2\sqrt{\pi/V} \right)^{2/3} \sqrt{L_0} \right) + \left( 2\sqrt{\pi/V} \right)^{2/3} L_0
\]

\[
\eta = 5.9 \text{ centipose}
\]

\[
\sigma = 0.83 \text{ J/m}^2
\]

Sintering Time for a Chain Aggregate

Sintering Time depends on the number of particle connections in a chain.

\[
t/d = \frac{2\eta}{3\sigma} (N - 1)^{0.68}
\]

by Frenkel (1945)

\[
t_{\text{Frenkel}} = \frac{2\eta d}{3\sigma}
\]

\[
\eta = 5.9 \text{ centipose}
\]

\[
\sigma = 0.83 \text{ J/m}^2
\]

Depends on the number of particle connections in a chain.
Fractal Dimension, $D_f$

$m \propto R^{D_f}$

$D_f = 1$

$D_f = 1.9$

$D_f = 3$

Fractal Aggregate
\( (D_f = 1.9) \)

- 66 particles
- \( T = 1500 \text{ K} \)
- 2.5 nm primary particles
Sintering time for fractal aggregate

Fractal Dimension, \( D_f \)

\[ m \propto R^{D_f} \]

- \( D_f = 1 \): wire
- \( D_f = 1.9 \): aerosol aggregates
- \( D_f = 3 \): compact

Monotonic increase w/ \( N_p \).

t decrease w/ \( D_f \).

\[ \frac{t}{d} = \frac{2\eta}{3\sigma} (N - 1)^{0.68} \]

\[ t_{\text{Frenkel}} = \frac{2\eta d}{3\sigma} \]

Fractal Dimension, $D_f$

$m \propto R^{D_f}$

- $D_f = 1$: wire
- $D_f = 1.9$: aerosol aggregates
- $D_f = 3$: compact

Monotonic increase w/ $N_p$.

t decrease w/ $D_f$.

$$t/d = \frac{2\eta}{3\sigma} (N - 1)^{0.68}$$

$$t_{\text{Frenkel}} = \frac{2\eta d}{3\sigma}$$

*J. Aerosol. Sci.** 38, 793 (2007)*
Sintering time for fractal aggregate

Fractal Dimension, $D_f$

$m \propto R^{D_f}$

- $D_f = 1$: wire
- $D_f = 1.9$: aerosol aggregates
- $D_f = 3$: compact

Monotonic increase w/ $N_p$.

$t$ decrease w/ $D_f$.

$t / d = \frac{2\eta}{3\sigma} (N - 1)^{0.68D_f}$

$t_{\text{Frenkel}} = \frac{2\eta d}{3\sigma}$

Vapor phase synthesis of nanoparticles

Nanoparticles are described as being sphere.
Plasma Synthesis

TEM images of cubic particles

Experiments by Kortshagen et al. at U of Minnesota

Precursor – 5% Silane (SiH₄) in Helium and Argon
Pressure – 2 torr
Power – 150 – 200 W
Frequency – 13.56 MHz
Chamber diameter – 5 cm
Length of filamentary discharge – 15 cm
Length of upstream uniform discharge – 5 cm

High-intensity plasma instability consists of filamentary plasma with individual plasma globules.

Distance between RF electrode and extraction orifice is 6 inch / 15 cm
Stability of Nanoparticles

Liquid

- Minimum surface area

Solid

- Crystal structure
- Surface structure
Bare surface to volume ratio
Transition from cube to truncated octahedron

- 2980 Si atoms
- 4 x 4 x 4 nm cube
Stability of Nanoparticles

Bare surface to volume ratio

Coated

Additional H energies

surface to volume ratio

PE / Si atoms

Assume: particle surfaces are covered by H
Etching of Spherical Particles

Sasaki et al., Vacuum 51, 537 (1998)

Experiment:
\[
\frac{R(100)}{R(111)} \approx 1.5
\]

MD simulation:
\[
\frac{R(100)}{R(111)} \approx 1.37
\]
Nanoparticle Based Devices

- building blocks

Assembly is a biggest challenge in Nanotechnology based device development.

- Microelectronic, optoelectronic devices
- Sensors

Need to control the location of particles in deposition process
Electrostatic Directed Assembly

- Charge patterns are unstable
- Stamp is easily damaged
- Non-insulated surface?

We want to have:

- Stable charge patterns
- Stable structure
- Adjustable charge strength
- Available and reliable technology

Use P-N junction
Silicon doped n-type GaAs substrate

1 µm Zinc doped p-type stripes and contacts are patterned by the photolithography plus ion implantation.

The Spacing between p-type stripes are 30µm in width

Monodisperse particles

$10^6$/cm$^{-3}$ & flow rate = 1 lpm

nozzle:

2mm in diameter & 1 cm above the substrate
Particles Deposition on PN

![Diagram showing particles deposition on PN junction](image-url)
P-N Model & Simulations

Experiment:

Simulation:
We can summarize the factors involved in the deposition process:

1. **External force, $F_{\text{ext}}$:**
   - Electrostatic ($F_e$), van der Waals ($F_{\text{vdw}}$) and image forces ($F_i$)

2. **Convective flow (only in x-direction)**

3. **Diffusion force (Brownian motion):** random, non-directional force
   
   $$F_{\text{diff}} = \left( \frac{6\pi \mu d kT}{C_c \Delta t} \right)^{0.5}$$

   $C_c$: slip correction factor

4. **Drag force, $F_D$:** to resist the momentum change
   
   $$F_D = \frac{3\pi \mu d v}{C_c}$$

   $v$: particle velocity

From Langevin Equation we can derive the particle trajectory: (in terms of velocity)

$$m_p \frac{dv}{dt} = F_{\text{ext}} + F_D + F_{\text{diff}}$$

$$v = v_0 e^{-\beta t} + \frac{F_{\text{ext}}}{m_p \beta} (1 - e^{-\beta t}) + B_1$$

$\beta=1/(\text{particle relaxation time})$

$$B_1 = \pm \left[ \frac{kT}{m_p} (1 - e^{-2\beta t}) \right]$$
Coverage selectivity increases as the reverse bias voltage increases.

Coverage Selectivity = \( \frac{C_N - C_P}{C_N} \times 100\% \)

Control location of particle deposition

Control coverage selectivity by voltage
Summary

Size of Nanoparticles.
- Hydrogen passivation surface prevented particle growth.
- Slowed sintering process & developed viscous flow model.

Shape of Nanoparticles.
- Hydrogen stabilizes Si crystals to be a cube.

Assembly of nanoparticles.
- Used P-N junction.
- Developed a Dynamics Model & Simulations.

Mechanics of nanoparticles.
- Sensitivity of morphology.
Summary

Acknowledgement

- Prof. M. R. Zachariah (U of Maryland & NIST)
- Dr. D. Tsai (Cabot Microelectronics)
- Prof. J. Zhu (U of Western Ontario, Canada)