Nanoparticle Synthesis and Assembly from Atomistic Simulation Studies

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Why Nanoparticle

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



tires & toners



• personal care & cosmetics

Proper manufacturing processes:

- improve cost
 improve quality

waste

- minimize waste
 provide safety

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



food



pharmaceuticals



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



	Nucleation	Rapid	
	of monomer	particle	Early stage
	via chemical	growth via	of very-
	or physical	coagulation	fine
	gas to	Particle	aggregate
	particle	number	formation
	conversion	decreases	

Collision & Sintering Time



Vapor phase synthesis of nanoparticles

sintering faster than collisions



Particle growth and morphology are determined by the competition of collisions and sintering



н

t_{collision} & t_{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

30ps



Contact Surface Area Analysis



Droplet interaction is proportional to the contact surface area.

Johnson *et al*. (1971) suggested

$$\pi a_0^2 \sim N_{atoms}^{4/9}$$





Reactivity of the Coated Particles



$$\frac{3}{2}kT = \frac{1}{2}mv^{2}$$
$$KE_{app} = \frac{1}{3}\frac{mv^{2}}{k}$$

- size ≯, harder to react
- No thermal reaction

- $t_{col} \rightarrow \infty$

Mathematical Model

Assumption



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

 $\Delta S = 4\pi a^2 \left[\Delta \theta (-\sin \theta) + O(\Delta \theta^2) \right] \qquad S: \text{ surface area}$

Energy balance

$$\frac{16}{3}\pi a^3\eta\gamma^2$$

Energy dissipation due to viscosity, η

$$=4\pi a^2\sigma\gamma$$

Work done by surface tension, σ

 σ = surface tension η = viscosity

 γ = velocity gradient

Effective passivation surface area



• $\xi=0$ towards the end

Mathematical Model

Solving the energy equation gives



$$t = \frac{2}{3} \eta d \int_{0}^{\pi/2} \frac{\sin\theta}{\sigma - \beta \xi(\theta)} d\theta$$

d = diameter = 2a

$$t_{\rm Frenkel} = \frac{2\eta d}{3\sigma}$$
 by Frenkel (1945)

Sintering (Bare vs. Coated)

(cross-section view)

6 nm droplets at 1500 K
KEapp = 110,000 K

120ps



Dynamics of Sintering

$$t = \frac{2}{3} \eta d \int_{0}^{\pi/2} \frac{\sin\theta}{\sigma - \beta \xi(\theta)} d\theta$$

 $\eta = 5.9$ centipose $\sigma = 0.83$ J/m²



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

Work done by relocation of surface atoms dominates the initial process

• $\sigma(\text{coated})/\sigma(\text{bare})=0.54$ Mb/Mc = 0.48

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

40 particle chain aggregate

T = 1500 K
2.5 nm primary particles



Sintering Time for a Chain Aggregate



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

$$A = -2\sqrt{3} \left\{ A \tan\left[\frac{1-2^{5/3}}{\sqrt{3}}\right] - A \tan\left[\frac{1-2\left(2\sqrt{\pi/V}\right)^{1/3}\sqrt{L_0}}{\sqrt{3}}\right] \right\},\$$
$$B = -2\left\{ \ln\left[1+2^{2/3}\right] - \ln\left[1+\left(2\sqrt{\frac{\pi}{V}}\right)^{1/3}\sqrt{L_0}\right] \right\},\$$
and
$$C = \ln\left[1-2^{2/3}+2^{4/3}\right] - \ln\left[1-\left(2\sqrt{\frac{\pi}{V}}\right)^{1/3}\sqrt{L_0}+\left(2\sqrt{\frac{\pi}{V}}\right)^{2/3}L_0\right]$$

Independent of primary particle diameter.

Universal relationship that only depends on chain length.

Phys. Rev. B 76, 054109 (2007)

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$$\eta = 5.9 \text{ centipose}$$

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

Number of Particles in a Chain

Excellent agreement with MD.

Phys. Rev. B 76, 054109 (2007)









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\eta = 5.9 centipose
\sigma = 0.83 J/m<sup>2</sup>
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Depends on the number of particle connections in a chain.



$$m \propto R^{D_f}$$



$D_{\rm f} = 1.9$



 $D_f = 3$



Fractal Aggregate $(D_f = 1.9)$

66 particles T = 1500 K 2.5 nm primary particles





 $m \propto R^{D_f}$

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





 $m \propto R^{D_f}$

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



Monotonic increase w/ Np.

t decrease w/ Df.

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

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



 $m \propto R^{D_f}$

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



Number of Particles in an Aggregate

Monotonic increase w/ Np.

t decrease w/ Df.

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

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SHAPE CONTROL

Vapor phase synthesis of nanoparticles

sintering faster than collisions



Nanoparticles are described as being sphere

Plasma Synthesis

TEM images of cubic particles



Stability of Nanoparticles

Liquid

Minimum surface area



Solid

Crystal structure Surface structure



Stability of Nanoparticles



Bare

surface to volume ratio

Transition from cube to truncated octahedron

2980 Si atoms 4 x 4 x 4 nm cube



Stability of Nanoparticles



Assume: particle surfaces are covered by H



surface to volume ratio

Additional H energies surface to volume ratio PE / Si atoms

Etching of Spherical Particles





PARTICLE ASSEMBLY



• building blocks



Assembly is a biggest challenge in Nanotechnology based device development.

- Microelectronic, optoelectronic devices
- Sensors (Ag) (Ag) (Ag) (Au) (Au) (Ag) (Ag) (Ag) (Ag)



Electrostatic Directed Assembly



- We want to have:
 - Stable charge patterns
 - Stable structure
 - Adjustable charge strength
 - Available and reliable technology



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



contacts are patterned by the photolithography plus ion implantation.

The Spacing between p-type stripes are $30\mu m$ 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











P-N Model & Simulations

We can summarize the factors involved In the deposition process:

1. External force, F_{ext}:

Electrostatic (F_e), van der Waals (F_{vdw}) and image forces (F_i)

2. Convective flow (only in x-direction)



3. Diffusion force (Brownian motion): random, non-directional force

$$F_{diff} = \left(\frac{6\pi\mu dkT}{C_c \Delta t}\right)^{0.5}$$

 C_c : slip correction factor

4. Drag force, F_D : to resist the momentum change

$$F_D = \frac{3\pi\mu dv}{C_c}$$
 v: particle velocity

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

$$m_{p} \frac{dv}{dt} = F_{ext} + F_{D} + F_{diff}$$

$$v = v_{0}e^{-\beta t} + \frac{F_{ext}}{m_{p}\beta}(1 - e^{-\beta t}) + B_{1}$$
Affected by electrostatic force

Affected by diffusion force

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

$$B_1 = \pm \left[\frac{kT}{m_p} (1 - e^{-2\beta t})\right]$$

Effect of Electric Field



Coverage selectivity increases as the reverse bias voltage increases

Control location of particle deposition

Control coverage selectivity by voltage

$$\frac{\text{Coverage}}{\text{Selectivity}} = \frac{C_N - C_P}{C_N} \times 100\%$$

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

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