## Nanoparticle Synthesis and Assembly from Atomistic Simulation Studies

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## Why Nenoparticle

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


- tires \& toners

- personal care \& cosmetics

- food


Proper manufacturing processes:

- improve cost
- minimize waste
- improve quality
- provide safety

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

## Paricle Synthesis

- Liquid Phase

- Easier to control size
- Production rate is low
- Vapor Phase

- High production rate $\checkmark$
Inexpensive!
- Difficult to control size

Challenge: Control size in vapor phase!

## Vapor phase synthesis of nanoparticles



| Nucleation |
| :---: |
| of monomer |
| via chemical |
| or physical |
| gas to |
| particle |
| conversion |

conversion

Rapid
particle
growth via
coagulation
Particle
number
decreases

Early stage
of veryfine
aggregate
formation

## 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

## Hydrogen Passivation Surface



H ${ }^{\prime}$


- Reactivity?
- Property?
- Sintering?


## $\downarrow$

$\mathrm{t}_{\text {collision }}$ \& $\mathrm{t}_{\text {sintering }}$

## Contents

- Size of nanoparticles
- Shape of nanoparticles
- Assembly of nanoparticles.


## SILE

COIVIROL

## Collision of H coatied particles (liquid \&: soliol)

## (cross-section view)

## 6 nm particles

 at 600 \& 1500 K30ps



## Contact Surface Area Analysis



$$
\begin{gathered}
\pi a_{0}^{2} \sim \mathbb{N}_{\text {atoms }}^{4 / 9} \\
\frac{3}{2} k T=\frac{1}{2} m v^{2} \\
K E_{a p p}=\frac{1}{3} \frac{m v^{2}}{k}
\end{gathered}
$$

## Reactivity of the Coated Particles

Critical approach energy for reaction


$$
\frac{3}{2} k T=\frac{1}{2} m v^{2}
$$

$$
K E_{a p p}=\frac{1}{3} \frac{m v^{2}}{k}
$$

- size $\boldsymbol{\pi}$, harder to react
- T $\boldsymbol{\pi}$, easier to react
- No thermal reaction
$-t_{c o l} \rightarrow \infty$


## Mathematical Model

## Assumption



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

Continuity

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

Energy balance


Energy dissipation due to viscosity, $\eta$

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

Work done by surface tension, $\sigma$
$\sigma=$ surface tension
$\eta$ = viscosity
$\gamma=$ 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


## Mathematical Model

## Solving the energy equation gives



$$
\begin{aligned}
& \beta=0 \text { (bare) } \\
& \beta>0 \text { (coated) }
\end{aligned}
$$

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

## Sintering (Bare vs. Coated)

(cross-section view)

6 nm droplets at 1500 K $\mathrm{KEapp}=110,000 \mathrm{~K}$


## Dynamics of Sintering

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

$$
\begin{aligned}
& \eta=5.9 \text { centipose } \\
& \sigma=0.83 \mathrm{~J} / \mathrm{m}^{2}
\end{aligned}
$$

6 nm particles at 1500 K


- $(\sigma-\beta) / \sigma=3.25^{*} 10 \wedge(-6)$ Work done by relocation of surface atoms dominates the initial process
- $\sigma($ coated $) / \sigma($ bare $)=0.54$

$$
\mathrm{Mb} / \mathrm{Mc}=0.48
$$

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

# 40 particle chain aggregatie 

## $\mathrm{T}=1500 \mathrm{~K}$ <br> 2.5 nm primary particles

## Sintering Time for a Chain Aggregate

Number of Particles in a Chain

## Universal relationship that only depends on chain length.

## Sintering Time for a Chain Aggregate



## Excellent agreement with MD.

## Sintering Time for a Chain Aggregate



Depends on the number of particle connections in a chain.

## Fractial Aggregate Sintering

Fractal Dimension, Df

$$
m \propto R^{D_{f}}
$$

## 

$D_{f}=1.9$


$$
D_{f}=3
$$


J. Aerosol. Sci. 38, 793 (2007)

## Frectal Aggregate ( $\mathrm{Df}=1.9$ )

66 particles
$\mathrm{T}=1500 \mathrm{~K}$
2.5 nm primary particles


## Stinfering tinne for fractal aggregate

Fractal Dimension, Df
$m \propto R^{D_{f}}$
$D_{f}=1$ : wire
$\mathrm{D}_{\mathrm{f}}$ = 1.9: aerosol aggregates
Df = 3: compact


Monotonic increase w/ Np.
$t$ decrease w/ Df.

$$
\begin{gathered}
t / d=\frac{2 \eta}{3 \sigma}(N-1)^{0.68} \\
t_{\text {Frenkel }}=\frac{2 \eta d}{3 \sigma}
\end{gathered}
$$

## Sinfering tinne for fractal aggregate

Fractal Dimension, Df

$$
m \propto \boldsymbol{R}^{D_{f}} \quad \begin{aligned}
& \mathrm{Df}_{\mathrm{f}}=1: \text { wire } \\
& \mathrm{Df}_{\mathrm{f}}=1.9: \text { aerosol aggregates } \\
& \mathrm{Df}_{\mathrm{f}}=3: \text { compact }
\end{aligned}
$$



Monotonic increase w/ Np. $t$ decrease w/ Df.

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$$

## SFLAPE <br> COIVIROL

Vapor phase synthesis of nanoparticles


Nanoparticles are described as being sphere

## Plasma Synthesis

## TEM images of cubic particles

Precursor - 5\% Silane $\left(\mathrm{SiH}_{4}\right)$ 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 $\mathbf{6}$ 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<br>$4 \times 4 \times 4 \mathrm{~nm}$ cube



## Stabiliy of Nanopanicles



Bare
surface to volume ratio

## Coated

Additional H energies
surface to volume ratio
PE / Si atoms

## Etching of Spherical Particles




Sasaki et al, Vacuum 51, 537 (1998)
Sasaki et al, Jap. J. Appl. Phys. 37, 402 (1998)


Experiment:

$$
\frac{R(100)}{R(111)} \approx 1.5
$$

MD simulation:

$$
\frac{R(100)}{R(111)} \approx 1.37
$$

> PMBIICLE ASCEIVIBLE

## 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
$1 \mu \mathrm{~m}$ Zinc doped p-type stripes and contacts are patterned by the photolithography plus ion implantation.

The Spacing between p-type stripes are $\mathbf{3 0 \mu m}$ in width

Monodisperse particles
$10^{6} / \mathrm{cm}^{-3}$ \& flow rate $=1 \mathrm{lpm}$
nozzle:
2 mm in diameter \& 1 cm above the substrate

## Pardicles Depostion on PN



## P-N Model \& Simulations

## Experiment:

nozzle


Simulation:


## P-N Model \& Simulations

We can summarize the factors involved In the deposition process:

## 1. External force, $F_{\text {ext }}$ :

Electrostatic $\left(\mathrm{F}_{\mathrm{e}}\right)$, van der Waals ( $\mathrm{F}_{\mathrm{vdw}}$ ) and image forces $\left(\mathrm{F}_{\mathrm{i}}\right)$

2. Convective flow (only in x-direction)
3. Diffusion force (Brownian motion): random, non-directional force

$$
F_{d i f f}=\left(\frac{6 \pi \mu d k T}{C_{c} \Delta t}\right)^{0.5} \quad C_{c}: \text { slip correction factor }
$$

4. Drag force, $\mathrm{F}_{\mathrm{D}}$ : to resist the momentum change

$$
F_{D}=\frac{3 \pi \mu d v}{C_{c}} \quad v: \text { particle velocity }
$$

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

$\beta=1 /($ particle relaxation time)

$$
B_{1}= \pm\left[\frac{k T}{m_{p}}\left(1-e^{-2 \beta t}\right)\right]
$$

## Effect of Eleciric Field



$$
\begin{aligned}
& \text { Coverage } \\
& \text { Selectivity }
\end{aligned}=\frac{C_{N}-C_{P}}{C_{N}} \times 100 \%
$$

## Summary

QSize of Nanoparticles.

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

QShape of Nanoparticles.

- Hydrogen stabilizes Si crystals to be a cube.

QAssembly of nanoparticles.

- Used P-N junction.
- Developed a Dynamics Model \& Simulations.

QMechanics of nanoparticles.

- Sensitivity of morphology.


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