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

U. Kortshagen
Department of Mechanical Engineering
University of Minnesota

Support: NSF through grants ECS-9731568, CTS-9876224, DGE-0114372 (IGERT)
University of Minnesota Supercomputer Institute
Overview

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

Electrons:
\[ v_e \approx O(10^6 \text{ m/s}) \]

Ions:
\[ v_i \approx O(10^3 \text{ m/s}) \]

Low pressure = Non-equilibrium

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

measured EEDF in Argon Plasma
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**
  \[\Rightarrow \text{Coagulation is suppressed.}\]
Single-crystal nanoparticles

A. Bapat\textsuperscript{1}, C. Perrey\textsuperscript{2}, Z. Shen\textsuperscript{3},
S. Campbell\textsuperscript{3}, C. B. Carter\textsuperscript{2}, U. Kortshagen\textsuperscript{1}

\textsuperscript{1}Mechanical Engineering
\textsuperscript{2}Chemical Engineering and Materials Sci.
\textsuperscript{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
$\sigma_g \sim 1.03-1.1$
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: \( \text{SiH}_4: \text{He}: \text{Ar} \) (typ.: 1:19:80)
- Total gas flow: 3-4 sccm
- Total gas pressure: 500-700 mTorr
- \( \text{SiH}_4 \) 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

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

courtesy of C. Perrey, C. B. Carter
“Cubic” nanoparticle showing [001] diffraction pattern of diamond-cubic Si.
Single-Crystal Nanoparticle

SEM of Si Nanoparticle

courtesy of C. Perrey, C. B. Carter
Single-Crystal Nanoparticle

Unstable “Capacitive” Discharge Mode
Single-Crystal Nanoparticle

Particles from Unstable “Capacitive” Discharge Mode
Single-Crystal Nanoparticle

High-Speed ICCD movie
Science Fiction??

Electrical contact to amorphous nanoparticles.

Work of Heiko Jacobs’ group.

courtesy of Z. Shen, S. Campbell
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\textsuperscript{1}, C. Perrey\textsuperscript{2}, J. Belich\textsuperscript{3}, C. B. Carter\textsuperscript{2}, J. Kakalios\textsuperscript{3}, U. Kortshagen\textsuperscript{1}

\textsuperscript{1}Mechanical Engineering
\textsuperscript{2}Chemical Engineering and Materials Sci.
\textsuperscript{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.
Set-up for ns-Si Film Growth
ns-Si films

ns-Si:H film deposited at 1450 mTorr.
Film Structure

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

Constant Photocurrent Method

- a-Si:H, 300 mTorr, 5W, 5% SiH₄/He (reference)
- ns-Si:H, 1450 mTorr
- ns-Si:H, 1800 mTorr
- ns-Si:H, 1500 mTorr

\( \alpha (\text{cm}^{-1}) \)

\( h\nu (\text{eV}) \)

Density of States

- Valance Band
- Band Tails
- Defect States
- Mobility Gap
- Conduction Band

\( e^{-h\nu/E_0} \)
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

Particle Growth in Plasmas

Nucleation

Coagulation

Surface growth

primary particle
Overview over Growth Model

\[
A + B = C + D
\]

NUCLEATION

Si\textsubscript{11-13}

RECTIONS

Si\textsubscript{1} ---- Si\textsubscript{10}

CLUSTERING

0.4 nm --------------------- 100 nm

PARTICLE GROWTH

PLASMA PARAMETERS AND FLOW

SECTIONS

1 2 3 4

180
Effect of Gas Temperature

3.8% SiH$_4$ in Ar, 117 mTorr

all reactions at 393K
only diffusion at 293K
Growth and Diffusion

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

“safe size”: particles negative no diffusion

primary particles

growth

diffusion

size = growth rate x time

survived diffusion
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.