Semiconductor Nanocrystals from Nonthermal Plasmas

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Nanocrystals in devices

- efficient light emitters and absorbers
- versatile deposition schemes
- possibility for flexible devices
- inexpensive to produce

www.nanosolar.com
Tan, et al., Journal of Applied Physics, 105, 2009
Outline

- Plasma synthesis and crystallization of silicon nanoparticles
- Control of surface properties
- SiNC-based LEDs
Plasma synthesis

Argon + SiH₄ (5:95 in Helium)

RF power: 13.56 MHz, 60-80W
Pressure: ~ 1.4 Torr (~180 Pa)
Gas flowrate: ~ 100 sccm
Surface-functionalizing SiNCs

As-produced silicon nanoparticles

Functionalization scheme

Result


photoluminescence quantum yield (QY)

\[
\frac{\text{# photons emitted}}{\text{# photons absorbed}}
\]
Plasma power and nanoparticle crystallinity

X-ray diffraction (XRD)

Raman spectroscopy

Crystallinity and photoluminescence

QY vs. plasma power

PL comparison: amorphous and crystalline nanoparticles

- Crystalline particles → efficient PL
- Amorphous particles → virtually no PL

Nanocrystal formation

Nonthermal plasma
\[ p = 100-200 \text{ Pa} \]
\[ T_{\text{electrons}} = 50,000 \text{K} \]
\[ T_{\text{ion, gas}} = 300 \text{K} \]


Particle temperature exceeds gas temperature
Nanoparticle crystallization: plan

1) **Synthesize** amorphous NPs of different sizes in first plasma

2) **Study** conditions necessary to crystallize them in second plasma

3) **Measure** plasma parameters – H density, ion density, electron temperature

![Diagram of synthesis and crystallization plasma with capacitive probe and OES](image)
Crystallization: 4 nm nanoparticles

Crystallization Power: 30 W

Amorphous nanoparticles (0 W 2nd plasma)

Nanocrystals (30 W 2nd plasma)

Nanocrystals (50 W 2nd plasma)
Crystallization: 4 nm nanoparticles

Crystallization Power: 30 W

Raman spectra

XRD patterns

Next: what are $n_H$, $T_e$, and $n_i$ required?
$n_H$ and $T_e$: Optical emission spectroscopy (OES)

\[
    n_H = n_{Ar} \frac{I_{i,H}}{X_{e,H}(E/N)R_{i,H}} \frac{X_{e,Ar}(E/N)R_{j,Ar}}{I_{j,Ar}}
\]

OES analysis: 4 nm nanoparticles

\[ T_e \sim 3.7 \text{ eV} \]
\[ n_H \sim 2 \times 10^{11} \text{ cm}^{-3} \]
Find $n_i$: capacitive probe measurements

**Probe**: driven by 1 MHz RF signal, modulated by square wave

**Capacitor**: discharge rate to ion flux

\[
\frac{dV}{dt} = \frac{eA_p \Gamma_i}{C_p}
\]

Capacitive probe measurements

\[ \frac{dV}{dt} = \frac{eA_p \Gamma_i}{C_p} \]

\[ \Gamma_i = n_i \left( \frac{k_b T_e}{M_{Ar}} \right)^{1/2} \]
Probe results – ion densities
Nanoparticle heating model

\[
\begin{align*}
G(T_p, \chi) - L(T_p, \chi) &= 0 \\
\Gamma_H^{in} - \Gamma_H^{out} &= 0
\end{align*}
\]

Steady-state model of \( T_p \)

**Energy balance:**
- \( G(T_p, \chi) \): Heating terms: \( \text{Ar}^+ + e \) reactions and H-based reactions
- \( L(T_p, \chi) \): Cooling terms: conductive heat transfer to background gas and H desorption

**Hydrogen balance:**
Incoming H flux = outgoing H flux

Nanoparticle heating model: results

Nanoparticles only reaching 100-200 K above room T
Crystallization cannot occur via thermal routes alone

Next: examine possibility of H-induced crystallization
Optimizing the Nanocrystal Surface

Sidearm gas injection

What is on the silicon surface?

Fourier-transform infrared spectroscopy (FTIR)

Si-$H_x$ stretch mode
Si-$H_x$ bend/wag mode
Injection gas experiment

Anthony, Rowe, Stein, Yang, and Kortshagen, Adv. Func. Mat., 2011
H₂ / Ar injection: QY and FTIR

Anthony, Rowe, Stein, Yang, and Kortshagen, Adv. Func. Mat., 2011

PL quantum yield

quantum yield (%)

percent H₂ partial pressure

Si-H₃, Si-H₂, Si-H

absorbance (a.u.)

wavenumber (cm⁻¹)

2200, 2100, 2000
H$_2$ / Ar injection: dangling bond density

Anthony, Rowe, Stein, Yang, and Kortshagen, Adv. Func. Mat., 2011
Hypotheses

Hypothesis 1:
Quench H-desorption

Hypothesis 2:
Improve H-coverage

$T_{\text{SINC}} \sim 100's \text{ of } K \text{ higher than } T_{\text{gas}}$
Gas injection: PL summary

PL spectra

- Hydrogen
- Helium
- Argon
- Deuterium

normalized PL intensity (a.u.)

wavelength (nm)

PL quantum yield

injected gas

argon | helium | hydrogen | deuterium

quantum yield (%)

Conclusion to hypothesis 1: quenching is important

Anthony, Rowe, Stein, Yang, and Kortshagen, Adv. Func. Mat., 2011
Gas injection FTIR: Si-H_x stretch region

Conclusion to hypothesis 2: H rxn is important

Anthony, Rowe, Stein, Yang, and Kortshagen, Adv. Func. Mat., 2011
Light-emitting Devices from Silicon Nanocrystals

Hybrid organic/inorganic light-emitting device

Electroluminescence

Cheng, Anthony, Kortshagen, and Holmes., *Nano Letters*, 2011
Device characteristics

External quantum efficiency = \frac{\text{# photons emitted}}{\text{# charges injected}} = \eta_{\text{injection}} \times \eta_{\text{internal}} \times \eta_{\text{extraction}}

Cheng, Anthony, Kortshagen, and Holmes., *Nano Letters*, 2011

peak efficiency: 8.6%
All-gas-phase LEDs
Green device manufacturing

Solution-phase device processing

Wet chemistry:
Pros:
• highly successful
• well-studied
• flexible
Cons:
• can be time-intensive
• requires multiple distinct steps
• spin-casting causes material loss
• solvents can be environmentally harmful

Can we develop a streamlined, green, gas-phase-only technique?

e.g., 1-dodecene

liquid-phase refluxing
215° C
All-gas-phase scheme

a) SiNC synthesis
b) Gas-phase functionalization
c) Film creation via impaction

Gas-phase capping

\[ H_2 + \text{alkene vapor} \]
Surface modification: FTIR

Impaction scheme

$P_{up}$: 1.4 Torr (180 Pa)

$P_{down}$: 0.23 Torr (30 Pa)

to pumps

Holman and Kortshagen, Langmuir, 2010
Film characteristics

\[
\frac{\rho_{\text{SiNC film}}}{\rho_{\text{bulk Si}}}
\]

density ratio

as measured using SEM + Rutherford backscattering

Film characteristics

SiNC-only light-emitting device

Electroluminescence

LED characteristics

peak efficiency > 0.02%

Summary

- Plasmas are effective for synthesis of high-quality nanoparticles
- Crystallization of nanoparticles does not occur through thermal routes alone
- Plasma effluent is highly reactive
- Gas-phase-only NC devices are viable
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