Novel Materials for Renewable Energy Applications : EFREE II

Overview

November 12, 2014

P Craig Taylor

Major Shared Facilities

- Synthesis Laboratory (nanoparticle capabilities)
- Clean Room (class 1000)
- Processing Laboratory (class 10,000)
- PECVD Laboratory
- Characterization Laboratory (optical, electronic, defect characterization)

Characterization Techniques

- Photothermal deflection spectroscopy
- Electron paramagnetic resonance
- Photoluminescence (PL)
- PL excitation spectroscopy
- Solar simulator (for PV cell testing)
- Optical absorption spectroscopy
- Raman spectroscopy
- Electron microscopy
- Many other techniques

Photothermal Deflection Spectroscopy (PDS)

Optical Absorption in a Nanocrystalline/Amorphous Si Composite

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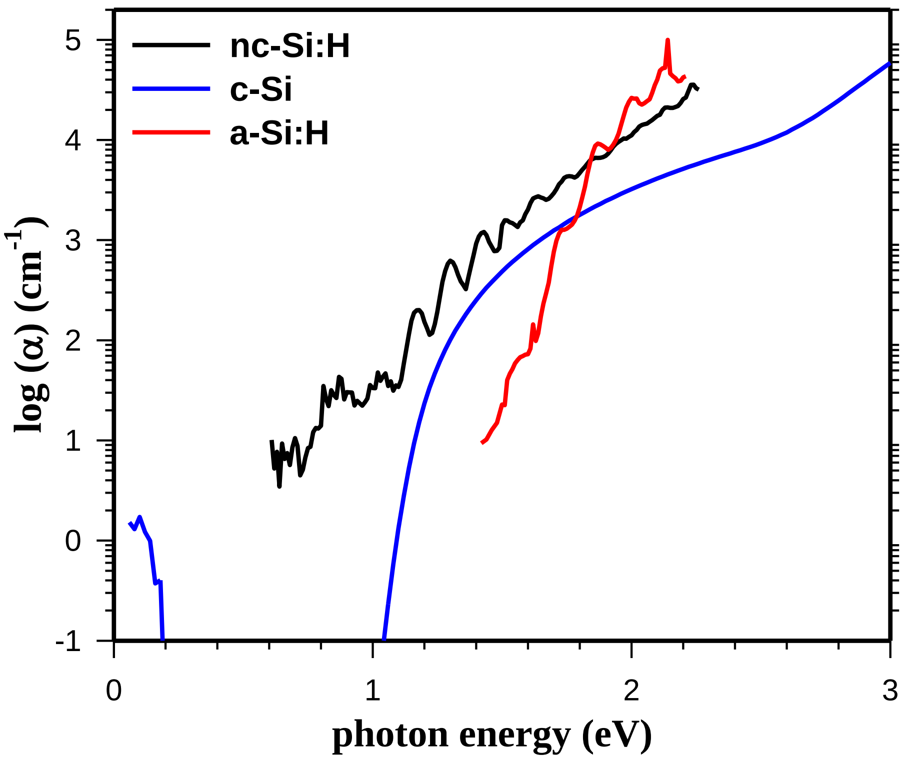

- 50 % volume fraction of ~6 X 20 nm nanocrystals
- Higher absorption at longer wavelengths in nc-Si:H
- No sharp drop-off of absorption in nc-Si:H

Electron Paramagnetic Resonance

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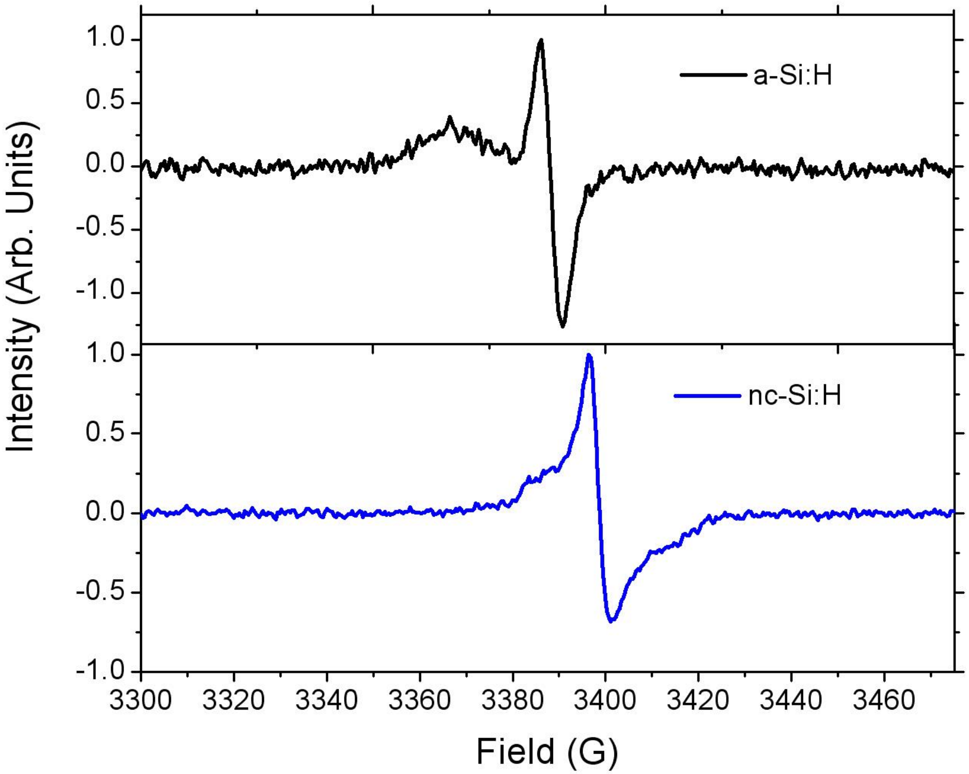
Comparison of LESR in *a*-Si:H and nc-Si:H

- CW YAG laser
- $T = 7$ K
- nc-Si:H: $g \approx 1.998$
  a-Si:H: $g \approx 2.005$

Same Signal Also Seen with Ar+ Laser



Why Study Exotic Forms of Si?

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30 years ago: Two forms of crystalline carbon
Now: An explosive growth in applications of carbon allotropes

Si is poised to undergo a similar transformation

Could drive the next 50 years of Si micro- and opto-electronics

The Potential of Metastable Phases of Silicon

- Direct band gaps and high extinction coefficients theoretically predicted
- Tunable band gaps covering important 1.5-2.5eV range
- "Stable" at temperatures appropriate for optoelectronic devices
- Novel synthesis to form macroscopic quantities of metestable phases demonstrated: Colloidal synthesis of high pressure BC8 phase, Solid state formation of clathrates

Direct Band Gap Silicon Allotropes

Qianqian Wang,[†,⊥] Bo Xu,[†,⊥] Jian Sun,[§,⊥] Hanyu Liu,[‡] Zhisheng Zhao,[‖] Dongli Yu,[†] Changzeng Fan,[†] and Julong He[*,†]

[†]State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, Hebei Province, China

[§]Department of Physics and National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China

[‡]Department of Physics and Engineering Physics, University of Saskatchewan, Saskatchewan, Canada, S7N 5E2

[‖]Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, United States

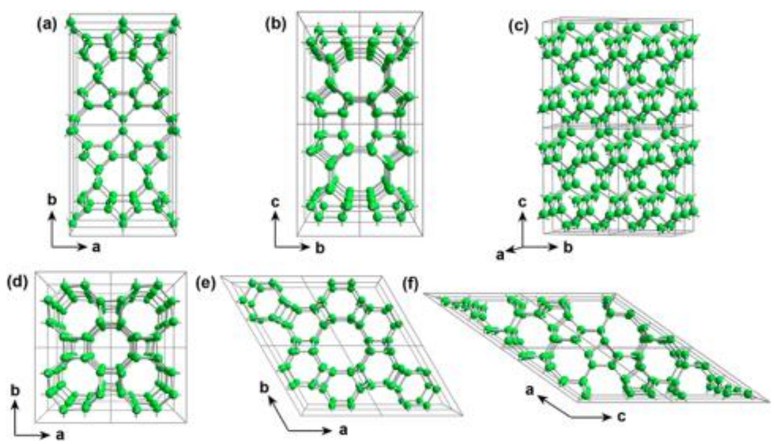
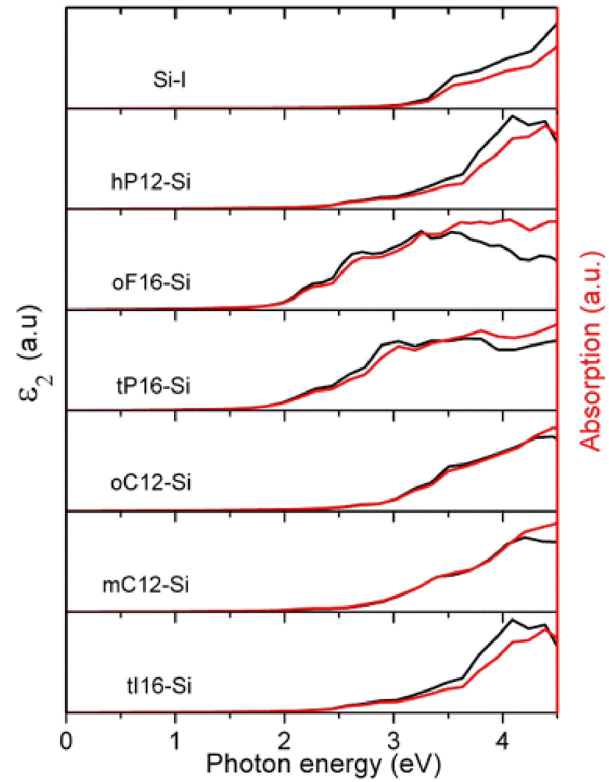
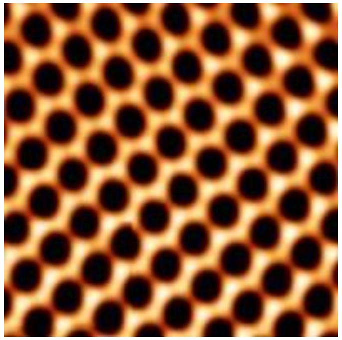


Figure 1. Crystal structures of (a) oC12-Si, (b) tP16-Si, (c) oF16-Si, (d) tI16-Si, (e) hP12-Si, and (f) mC12-Si.

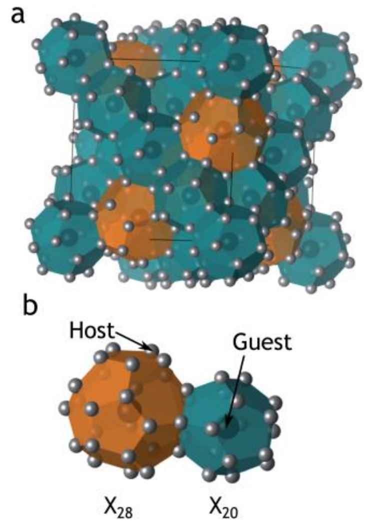


Characterization of Optical and Electronic Properties

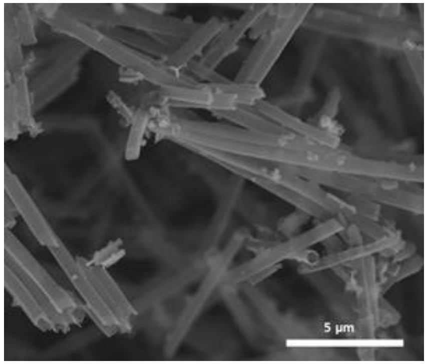
- BC8 Si
- Si_{24}
- Clathrate Si
- Nanocrystalline Si
  - Self standing
  - In amorphous matrices
- Alloys with C, Ge …
- Other structures
  - Carbon-based nano- and meso-materials



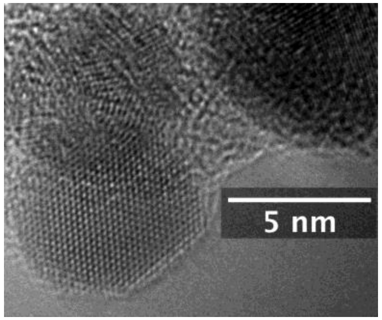
Silicene



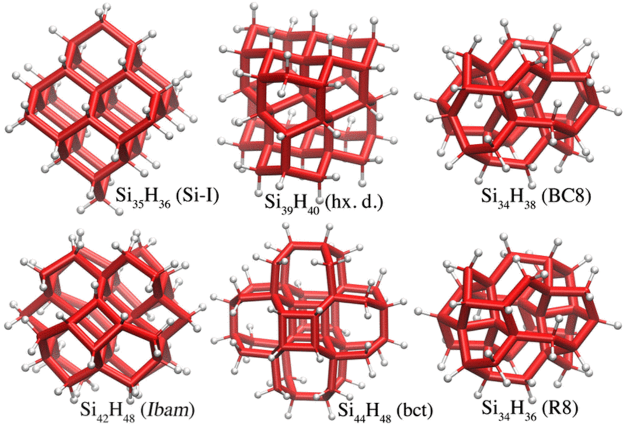
Si Clatharate



Si Nanotubes



Si Quantum Dot

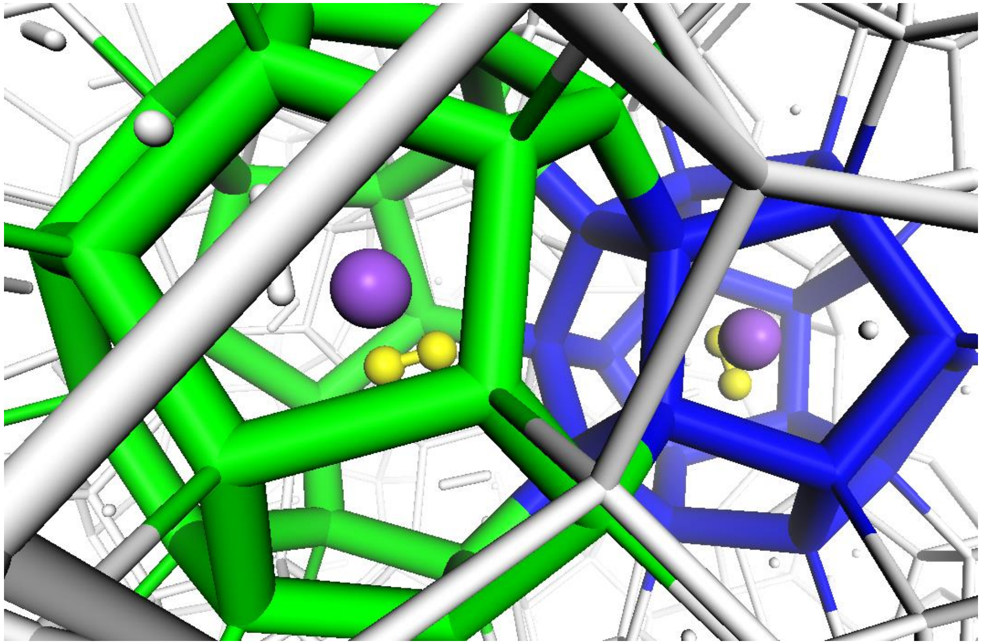


High Pressure Phases of Silicon

Clathrate Si

Transfer of basic discoveries

- Clathrates for Renewable Energy Applications



Seeds Spawn New Transformative Programs

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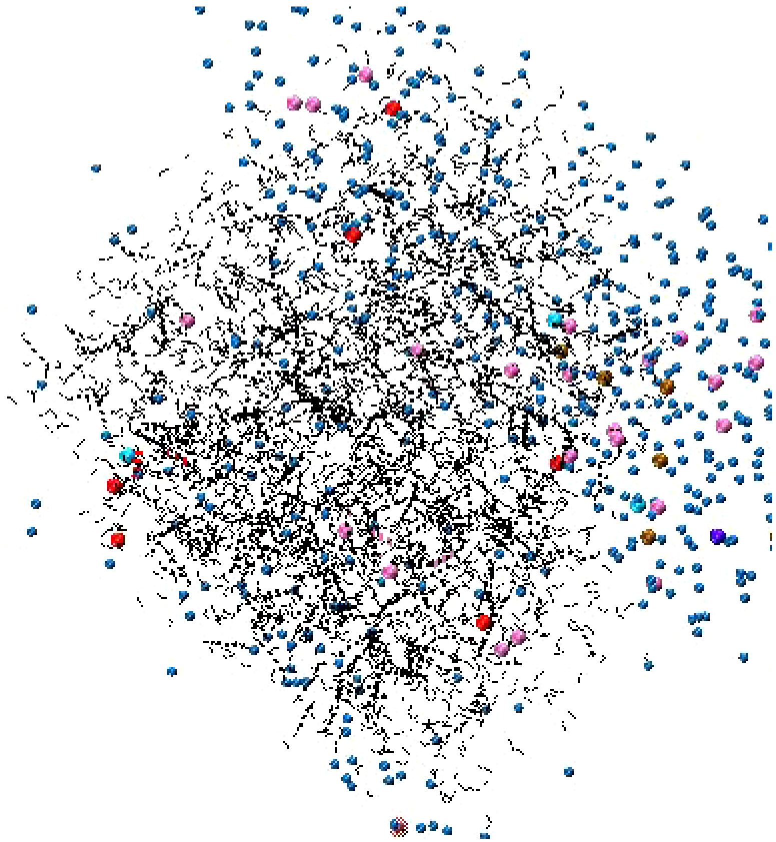

Walsh, M. R.; Koh, C. A.; Sloan, E. D.; Sum, A. K.; Wu, D. T., “Microsecond Simulation of Spontaneous Methane Hydrate Nucleation and Growth” *Science*, **2009**, 326 (5956), 1095-1098.

Seeds Spawn New Transformative Programs

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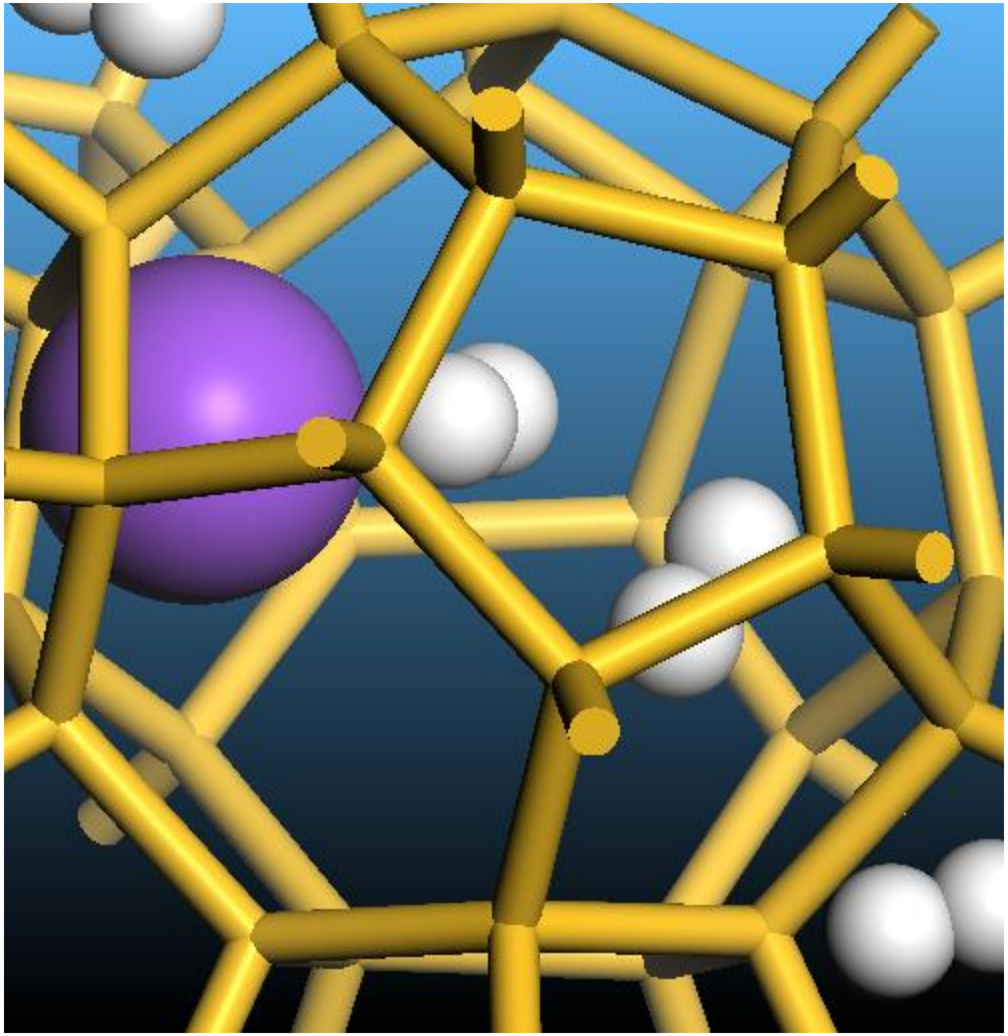
Molecular Hydrogen Stored in Clathrate Si

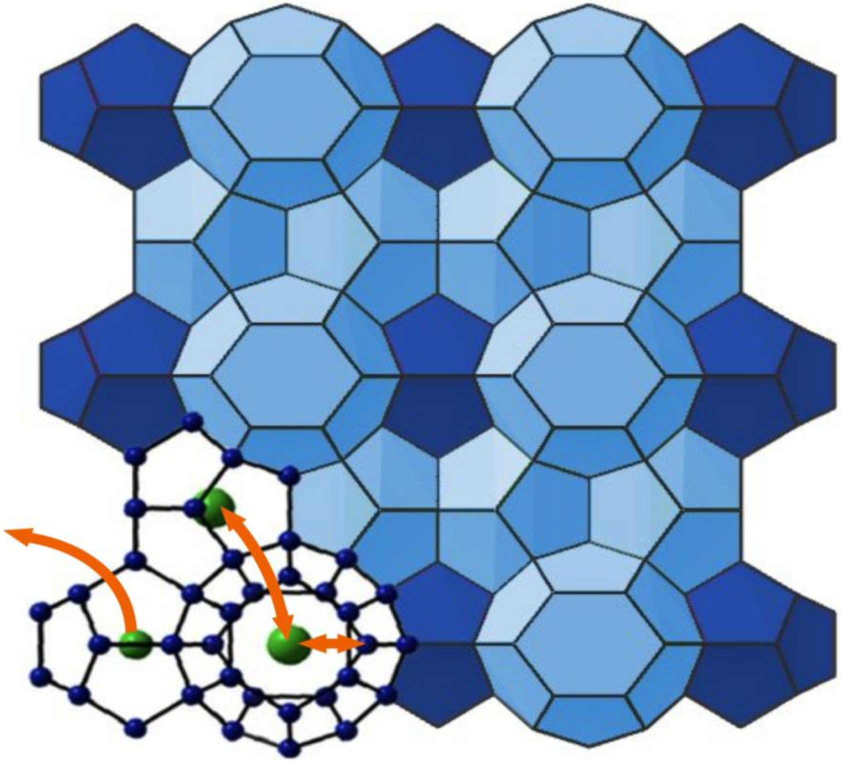
- Structure nucleates around Na atoms
- Storage is reversible



Video courtesy of Mark Lusk

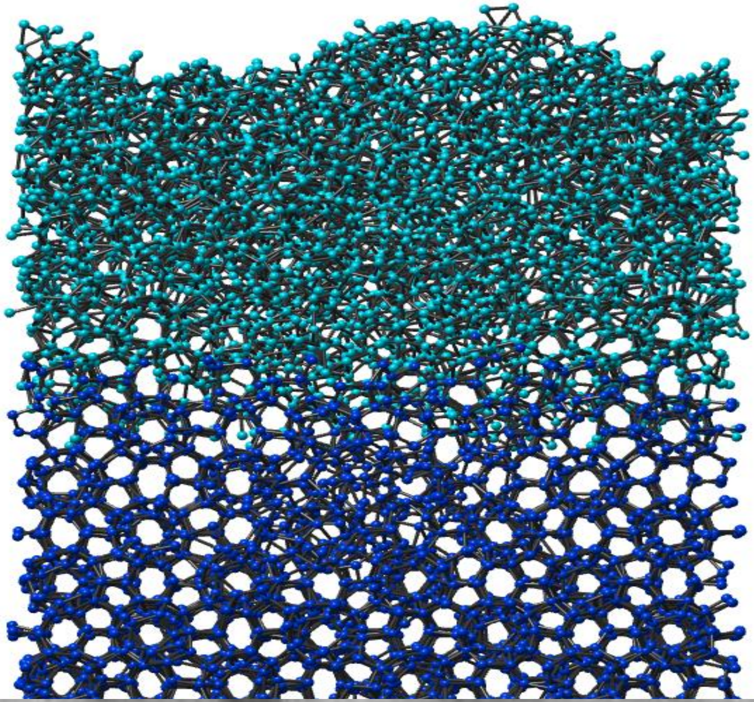
Background

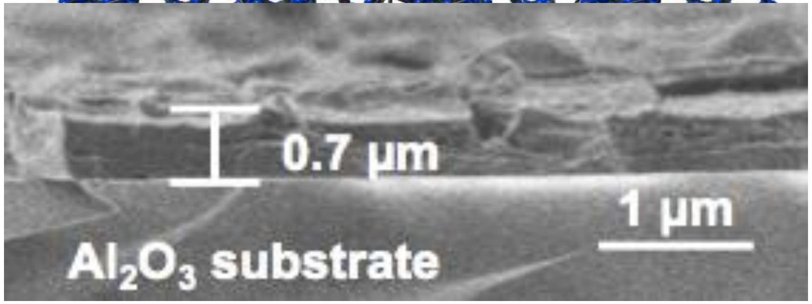
Clathrate frameworks are built from covalently bound cages connected in 3D. Guest ions (green spheres) reside within the void space in these cages. Arrows indicate guest-guest and guest-host interactions & guest mobility



Theoretical Component

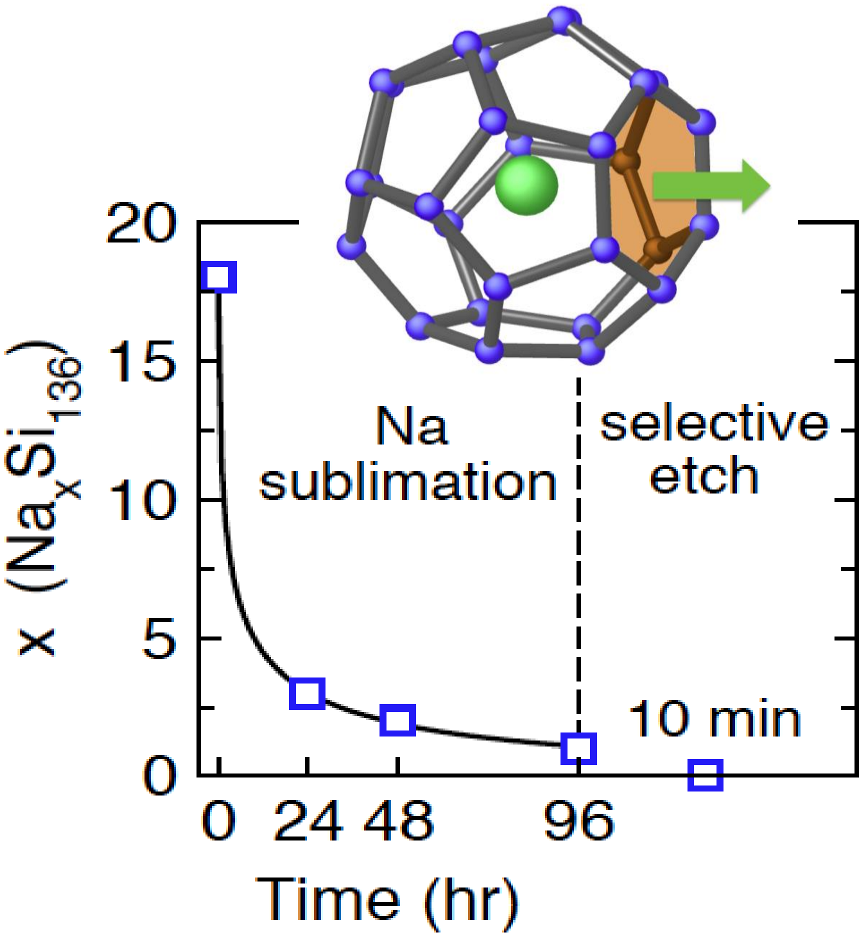
Top: MD simulations can reveal the transformation mechanism from amorphous (upper layer) to clathrate (lower layer) structures. *Bottom:* Si_{136} clathrate thin film grown on sapphire.





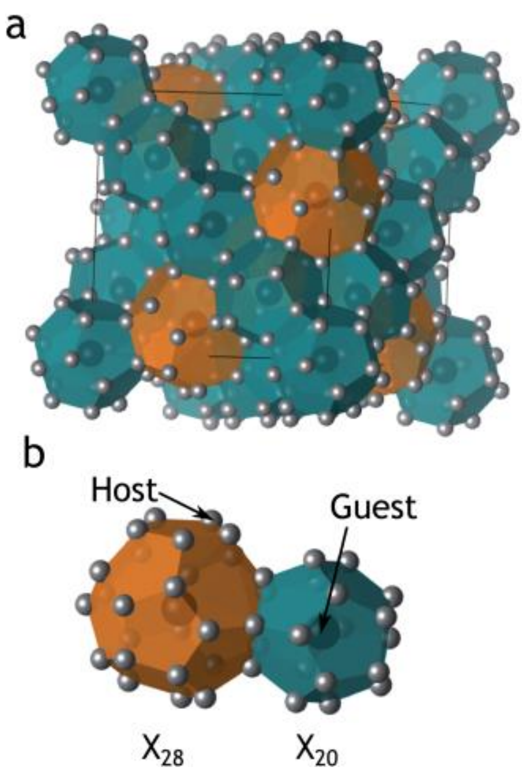
Na removal

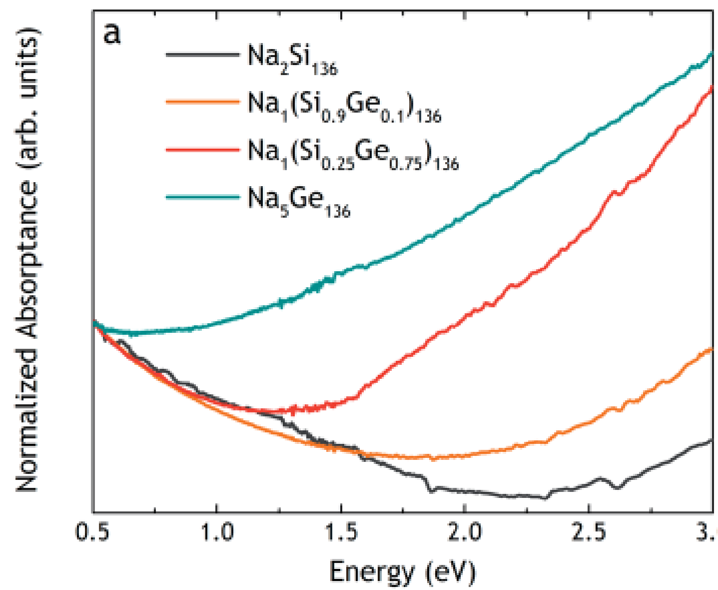
Experimental Na guest removal by sublimation and etching, indicating Na motion is facile in the Si_{136} framework.



Synthesis and optical band gaps of alloyed Si–Ge type II clathrates†

Lauryn L. Baranowski, Lakshmi Krishna, Aaron D. Martinez, Taufik Raharjo, Vladan Stevanović, Adele C. Tamboli and Eric S. Toberer*





Silicon Clathrate Summary

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Growing and characterizing the clathrate form of silicon has tremendous potential to dramatically transform microelectronics and opto-electronics in the 21st century

BC8 Si

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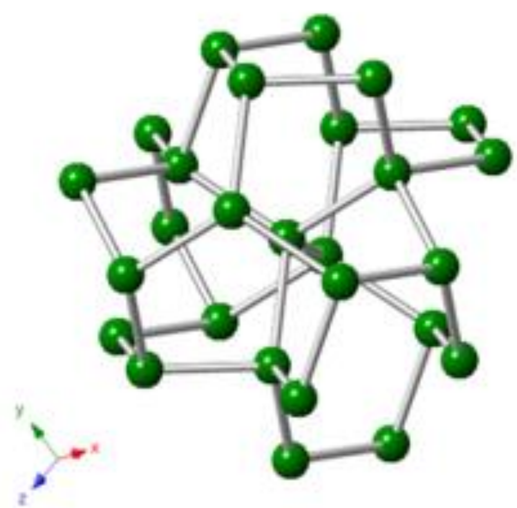
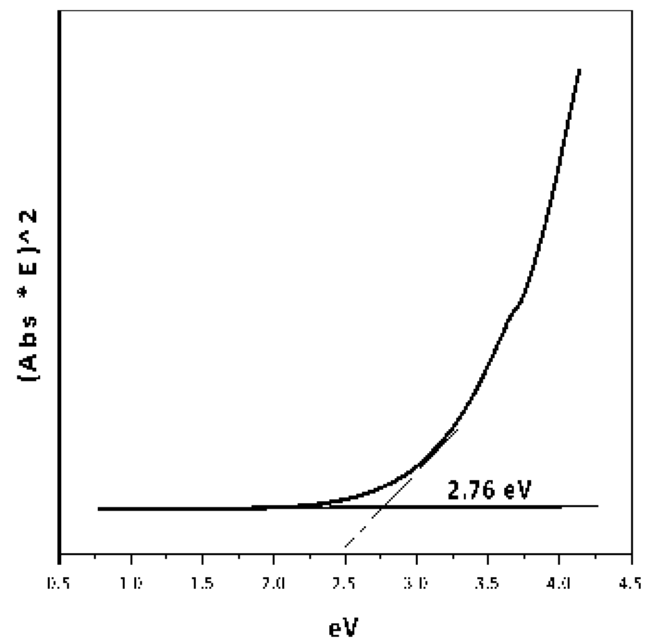
Colloidal Synthesis of an Exotic Phase of Silicon: The BC8 Structure

Shreyashi Ganguly, Nasrin Kazem, Danielle Carter, and Susan M. Kauzlarich*

Department of Chemistry, University of California, Davis, California 95616, United States

S *Supporting Information*



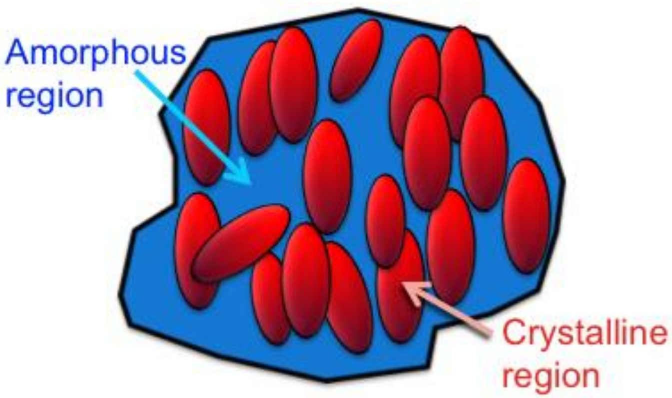


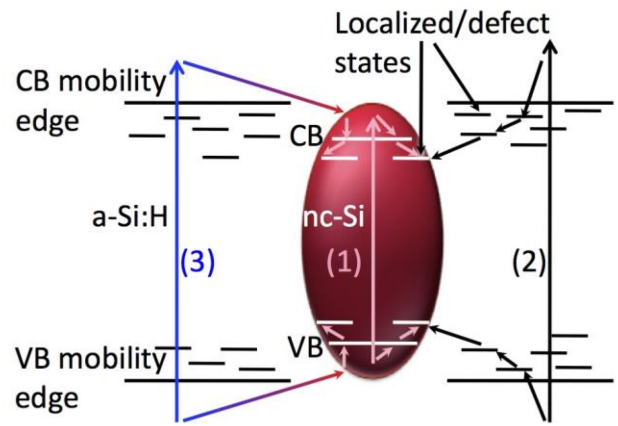
Nanocrystalline Si

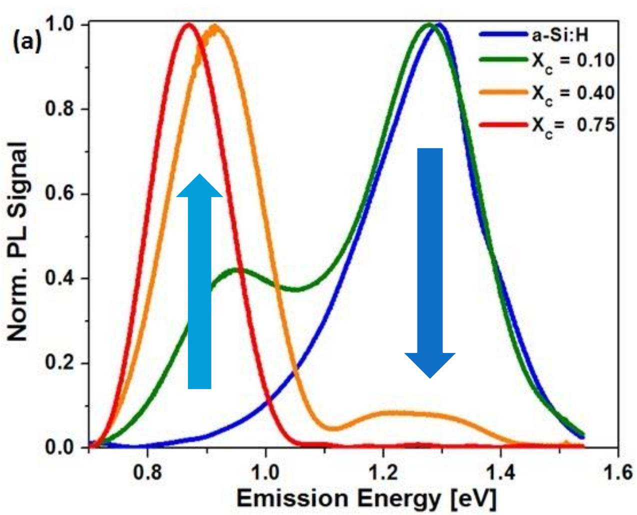
Nanocrystalline Si

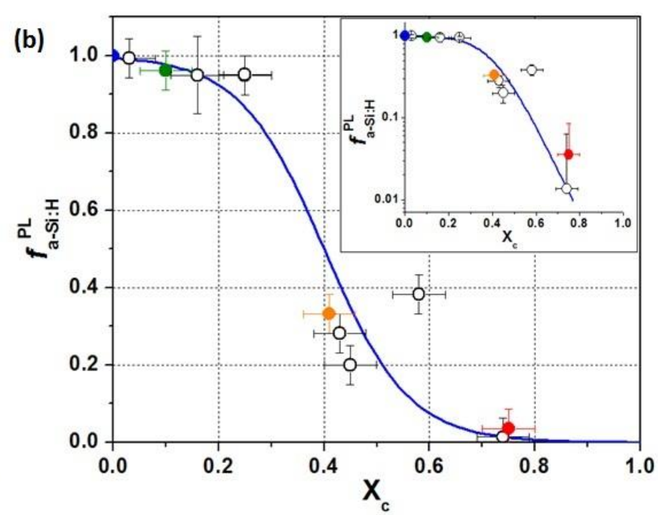
Nanocrystalline Si (2-4 nm diameter) being removed from the reactor.

Hot Carrier Transfer: Conventional nc-Si:H







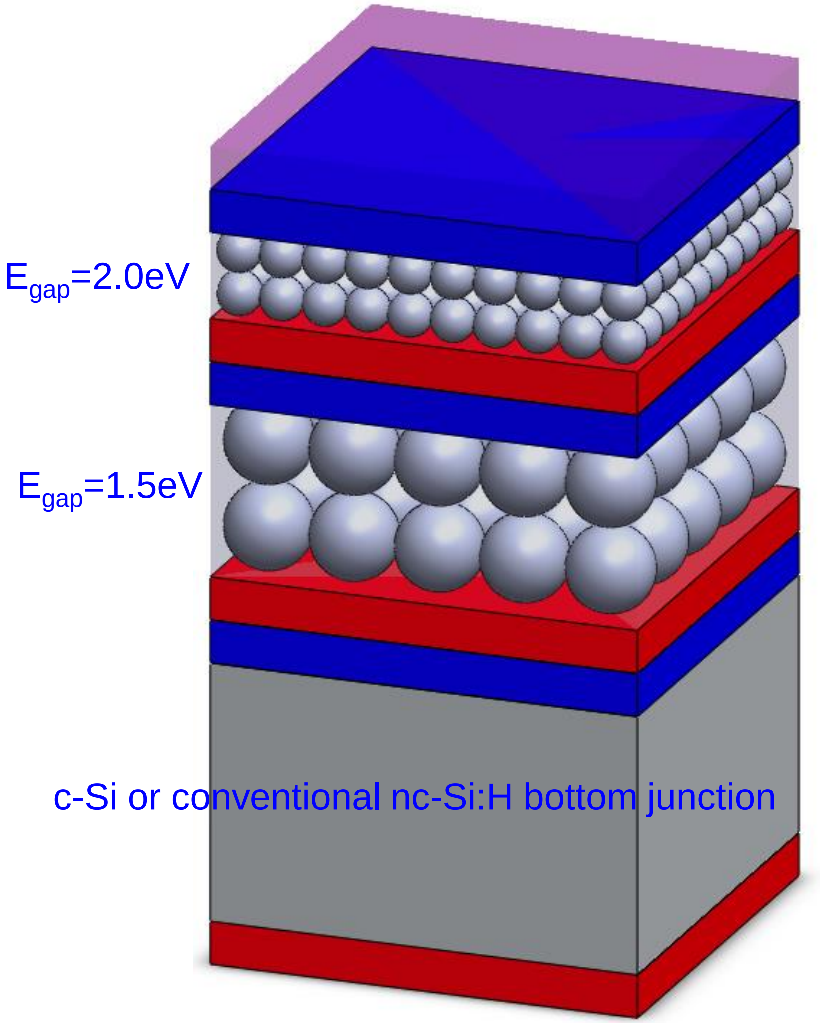


Objective

An integrated theoretical and experimental approach

“Engineered” Nanocrystalline Si that takes advantage of hot carrier transfer to:

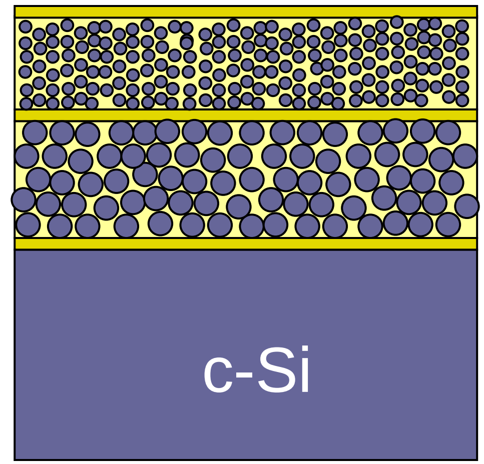
- Tune band gap through crystallite size and amorphous matrix properties
- Increase photostability
- Improve doping efficiency
- Improve mobility
- Achieve single junction efficiencies and stability not possible with conventional “thin film Si”
- Create high efficiency, stable, SiNP-based multijunction cells
- Explore the potential for true hot carrier architectures that exceed the Shockley-Queisser limit



Plasma Synthesized Si Quantum Dots

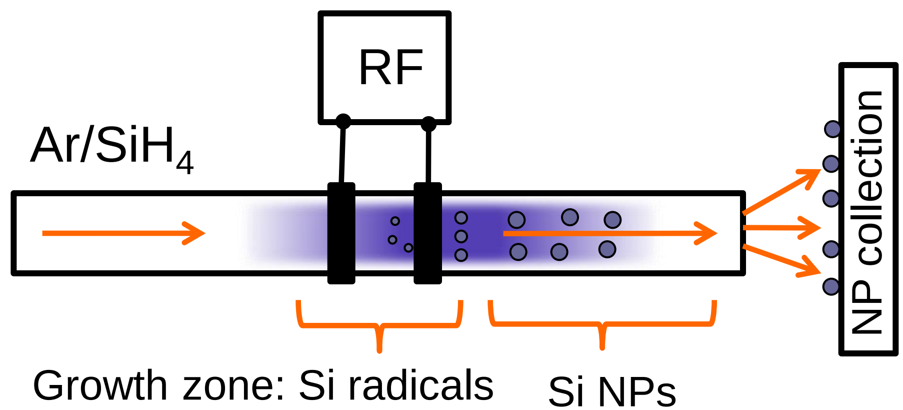
Goal - Si quantum dots with:

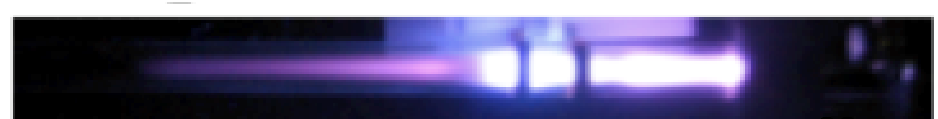
- Control of dot size
- Narrow size distribution
- Controlled surface properties
- Mechanisms for assembly into films
- High throughput synthesis



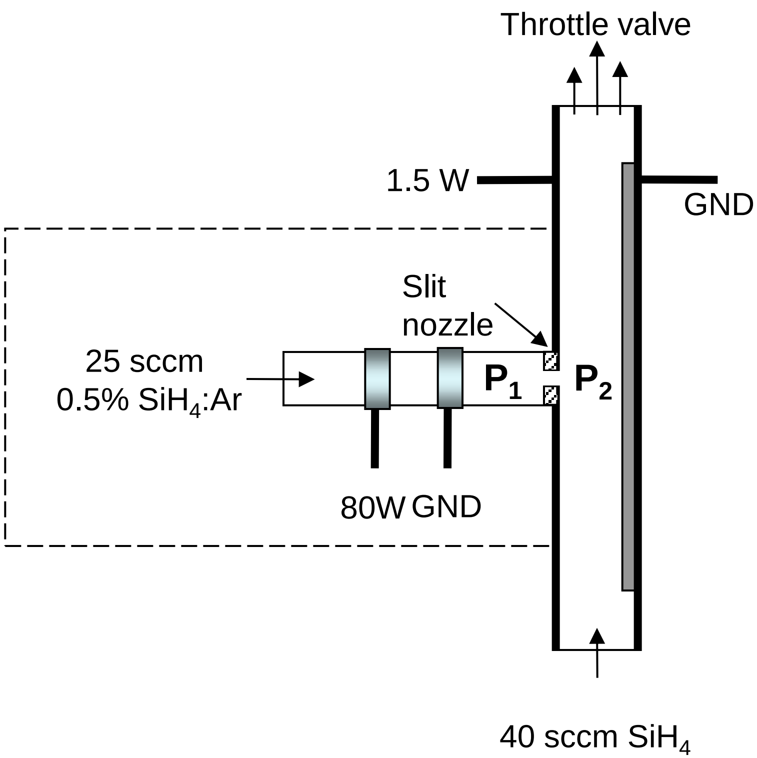
Our approach: Si nanoparticle growth by continuous-flow PECVD

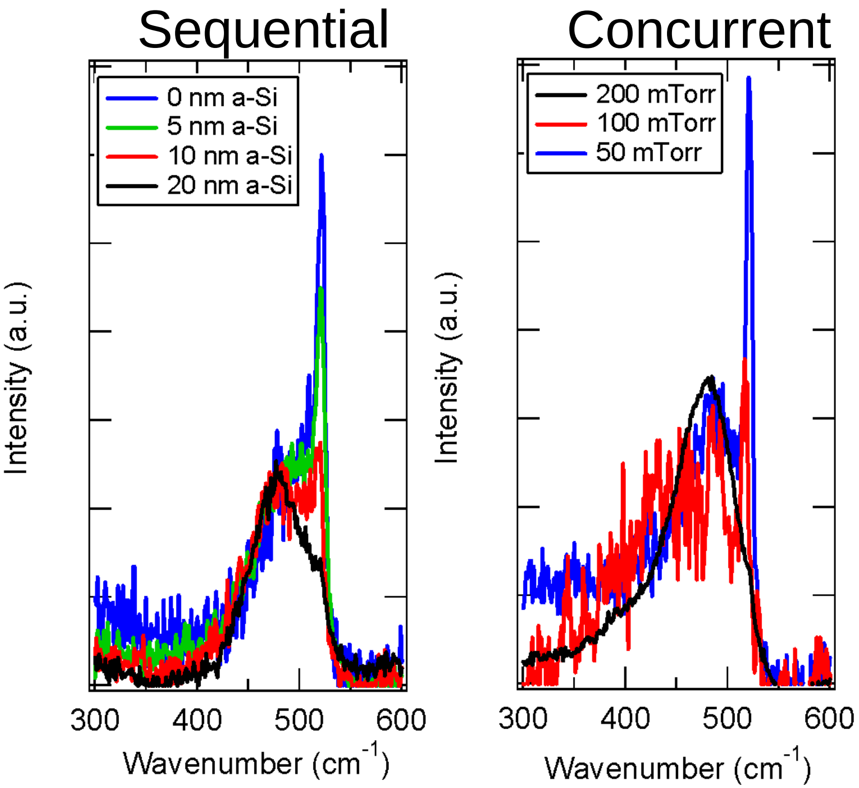
- Dilute SiH_4/Ar plasma
- Highly exothermic surface reactions heat particles – nucleation and growth of crystalline Si
- Collect downstream
- Passivate and assemble in colloidal phase or
- Gas-phase processing downstream; embed in matrix





Sequential and Concurrent Deposition

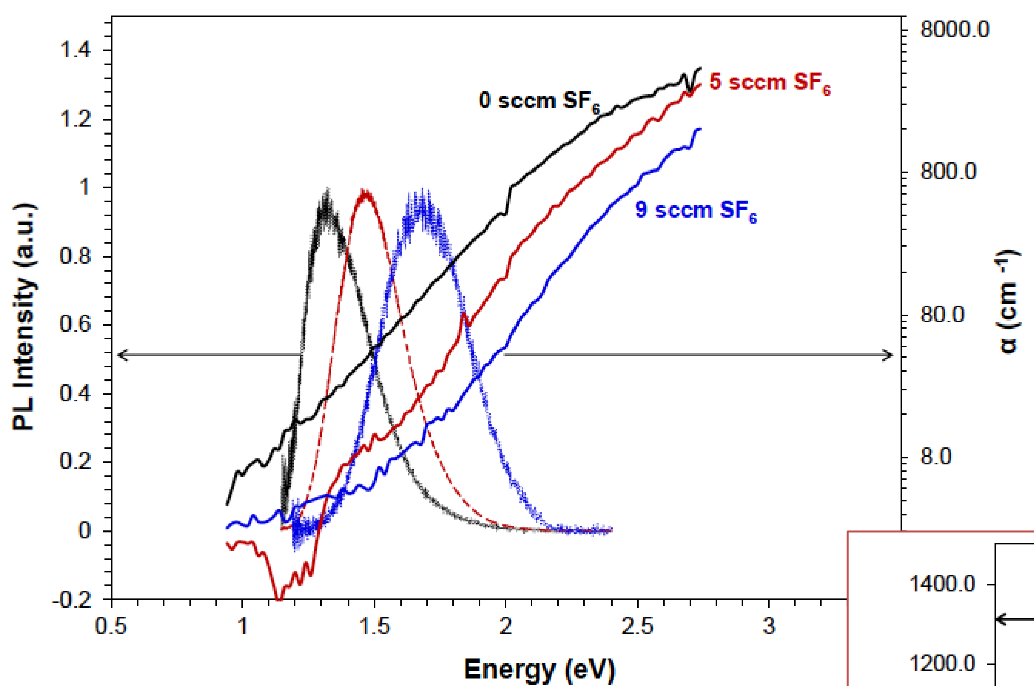




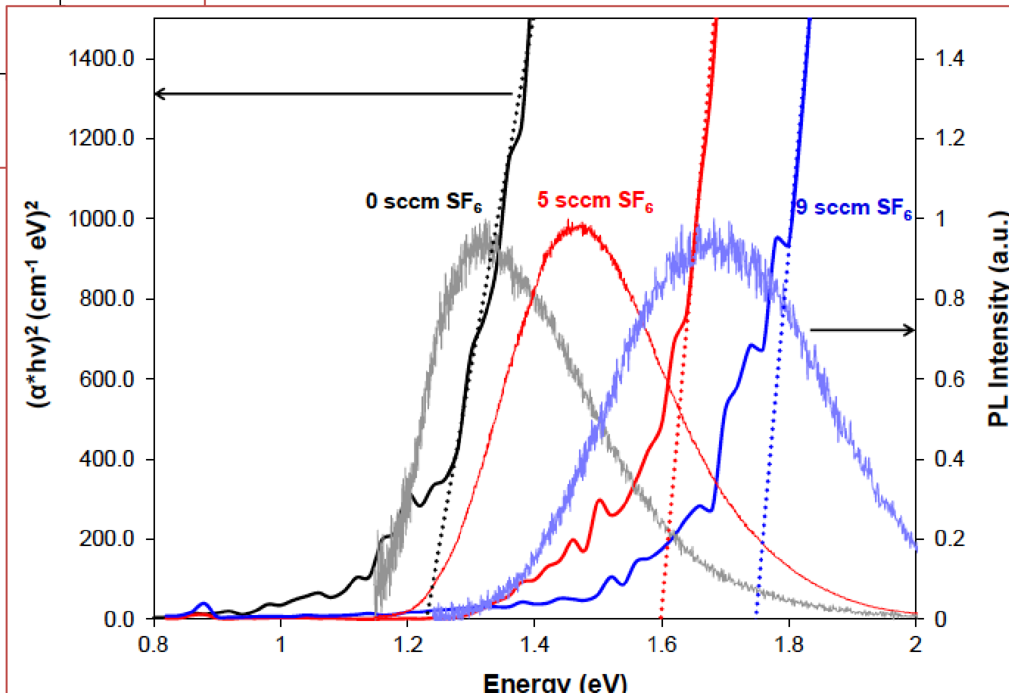
Crystal fraction:

- Sequential growth – controlled by varying the deposition times of each layer
- Concurrent growth – P_2 (PECVD) controls the exit velocity of the SiNPs and therefore the crystalline fraction

Absorption spectrum and PL of SF_6 treated isolated Si nanoparticles

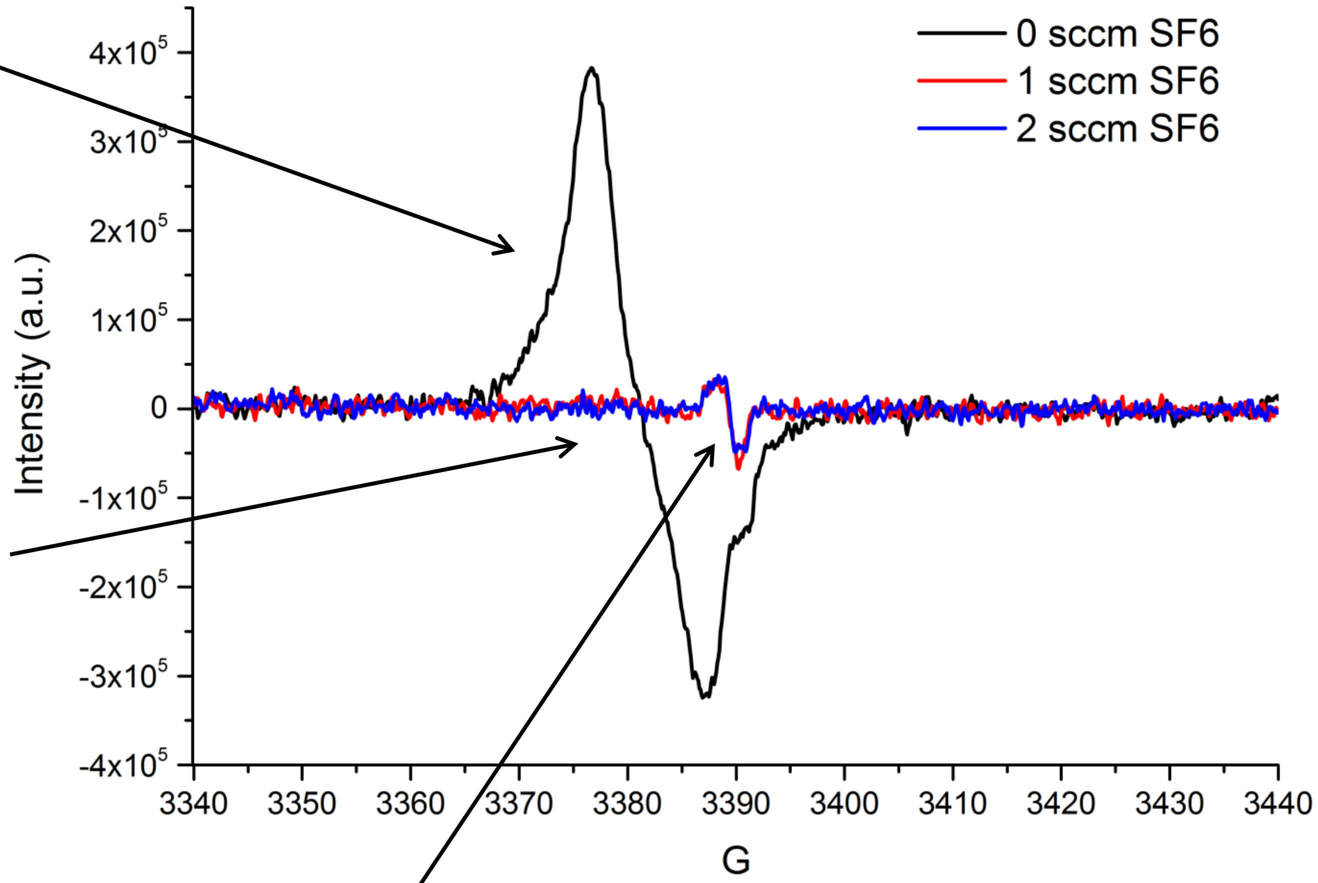


Tauc plot shows bandgap increases with increased SF_6



ESR of Oxidized SF6 Treated SiNPs

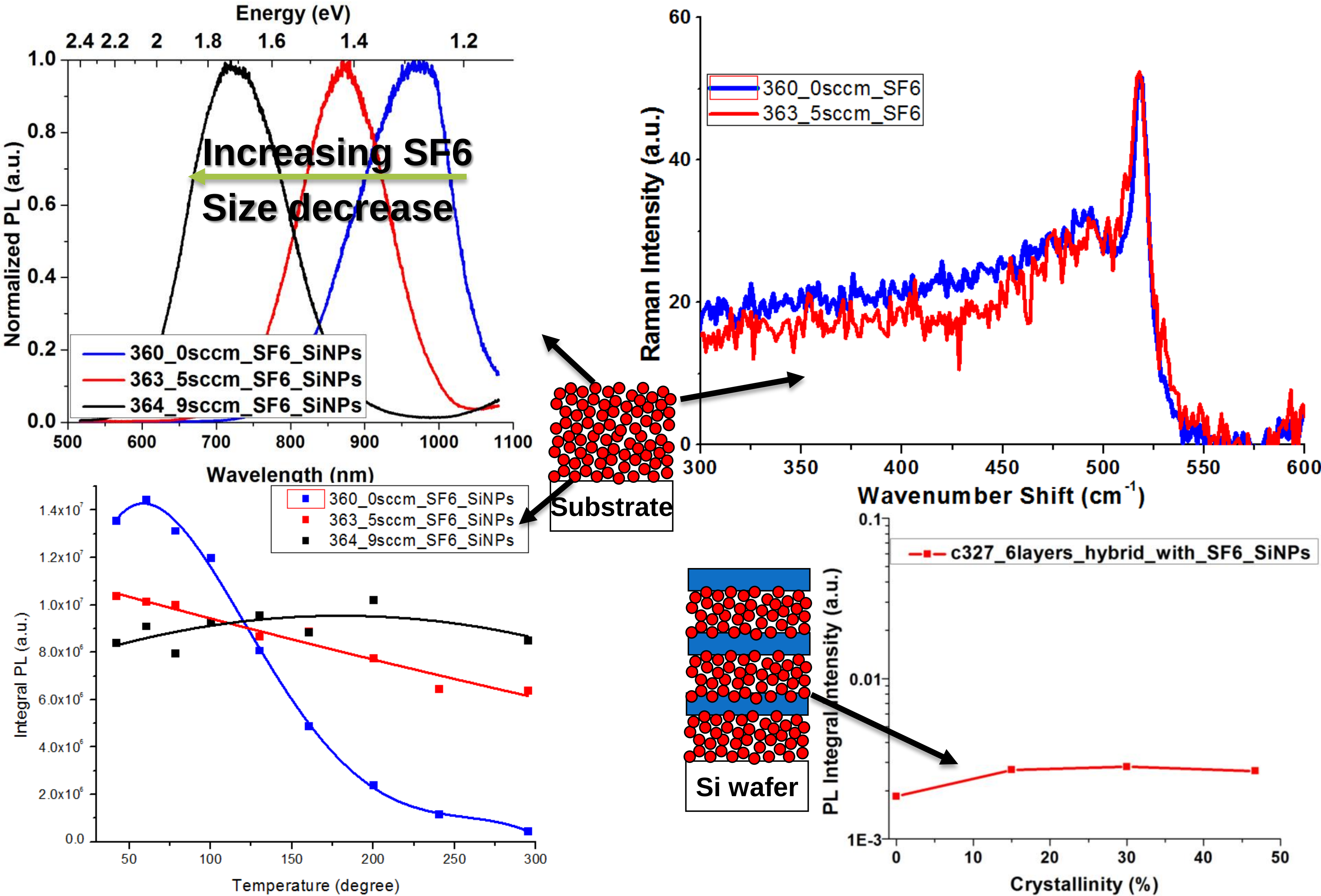
Large signal shows high level of crystalline defects in untreated SiNPs



Signal is not present in SF6 treated samples, suggesting significant decrease of defects on surface

Small signal to the right signifies defects in oxide layer for treated and untreated samples

SF6 treated SiNPs and Hybrid Structure with SF6 treated SiNPs



Si nanowires

Sn Seeded, PECVD Grown Si Nanowires

Vapor-Liquid-Solid growth by CVD

- Au is the most common catalyst
- Growth temperatures 600-900ºC

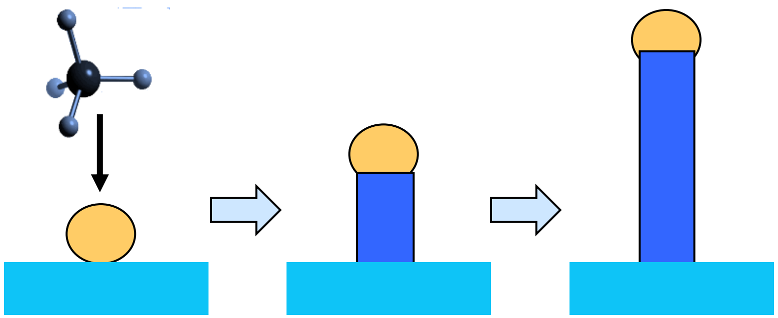
Sn Seeds

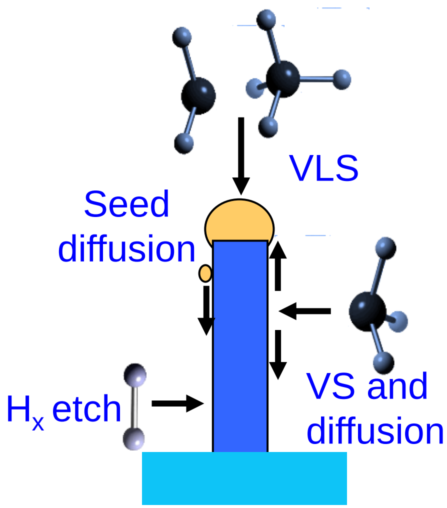
- Sn isovalent
- Eutectic T = 232º C (Au: 363º C)
- Si solubility < 10^{-4} (Au: 18%)

PECVD

- a-Si:H and nc-Si
- Lower processing temperatures
- Sn seeds formed by H_2 plasma reduction of SnO_2 coated glass

PECVD and/or Sn seeds not extensively studied





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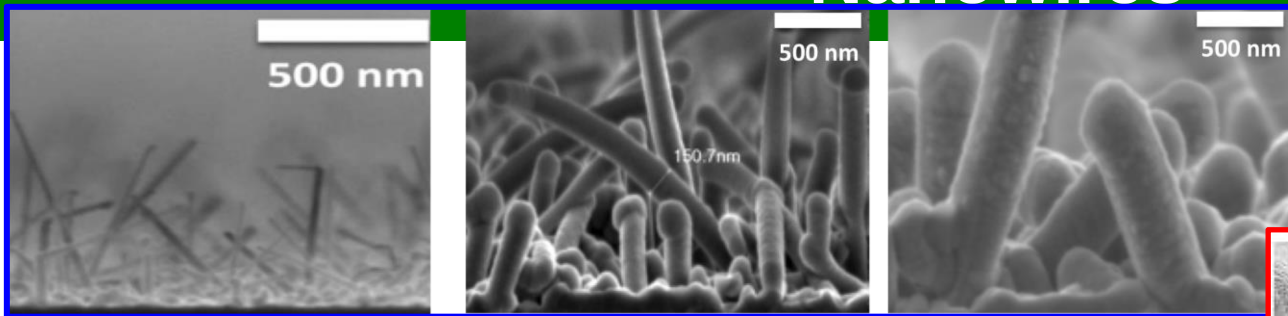
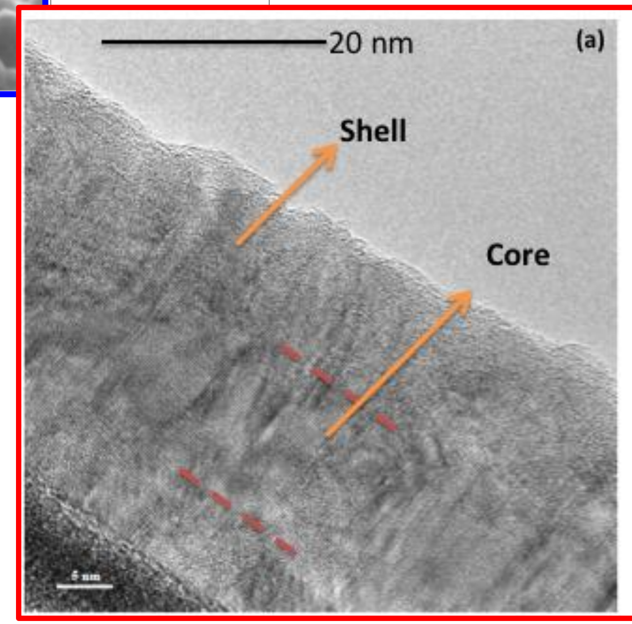
Sn Seeded, PECVD Grown Si Nanowires



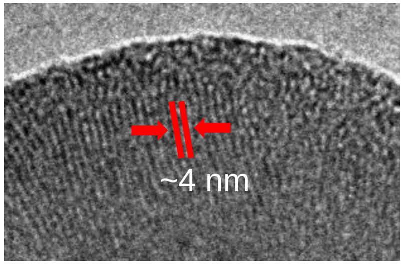
2 mins 20 mins 40 mins

Growth duration



- Wires grow at 280º C - 400º C
- Crystalline Core – VLS growth
- Nanocrystalline shell – VS growth
- Sn etched by H_2 plasma, possibility of metal free wires
- Electro-assisted micelle self-assembled template for true “nano”wires

SEM of nano silica template



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Membranes

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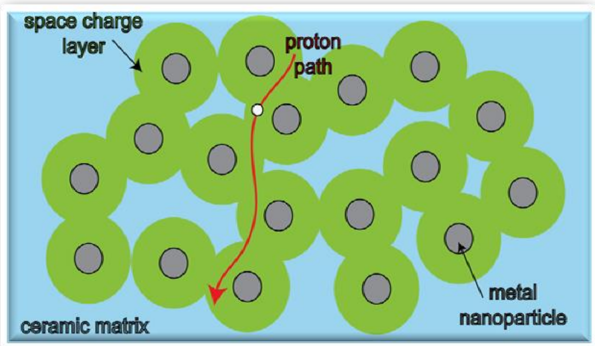
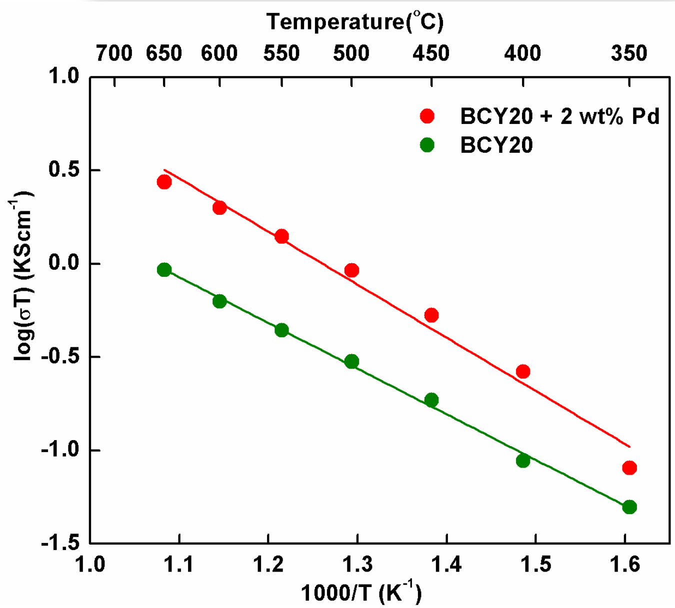
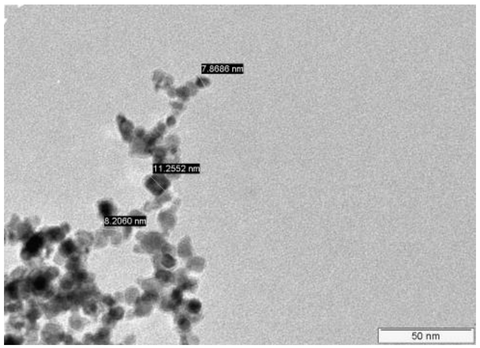
Macroscopic effect of nano sized particles

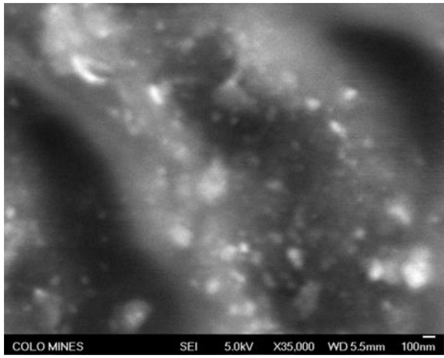
Super ionic hybrids
Pd nano particles in BCY20

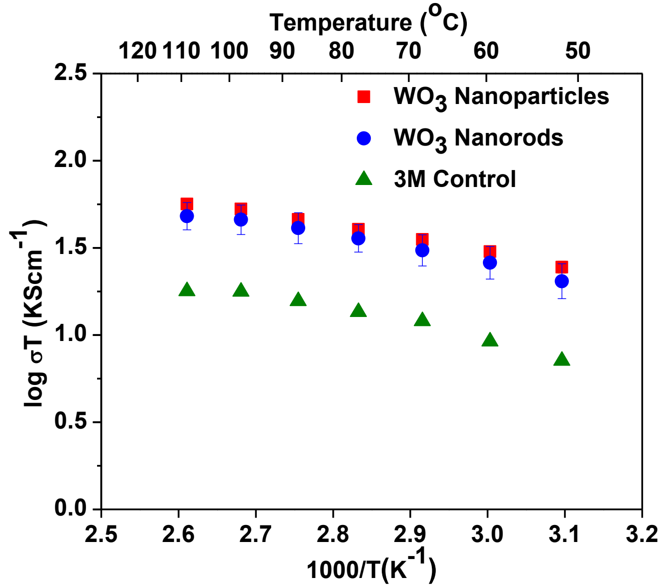




Tungsten oxide nanoparticles and nanorods in 3M ionomer







Significance: Incorporation of appropriate nano particles in both high/low temperature ion conductors significantly enhances protonic conductivity

Sun Edison/EXCEL Facility
Alamosa, CO

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