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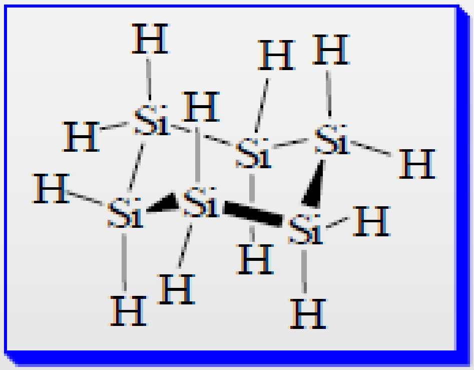
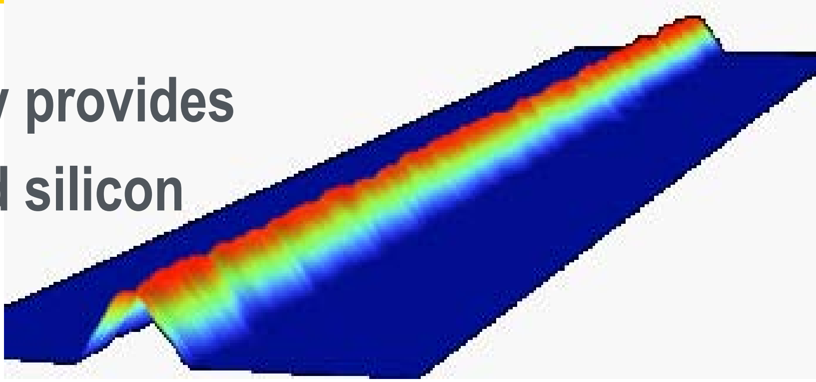
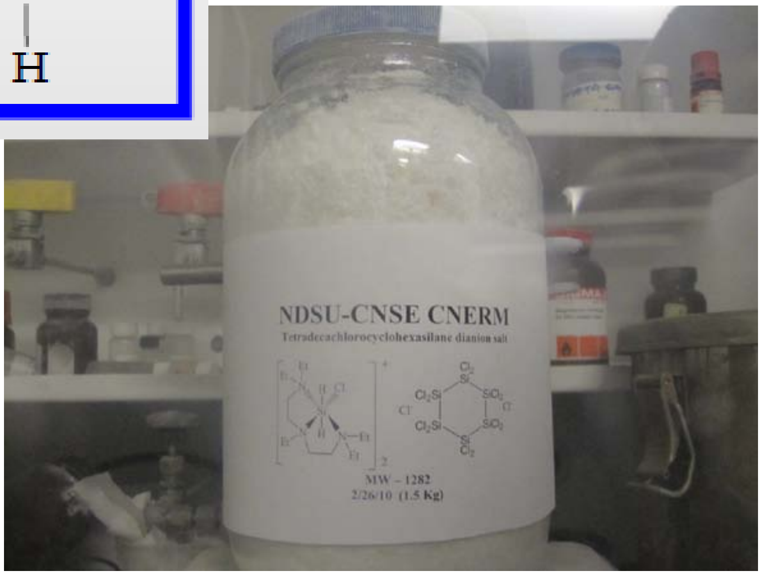
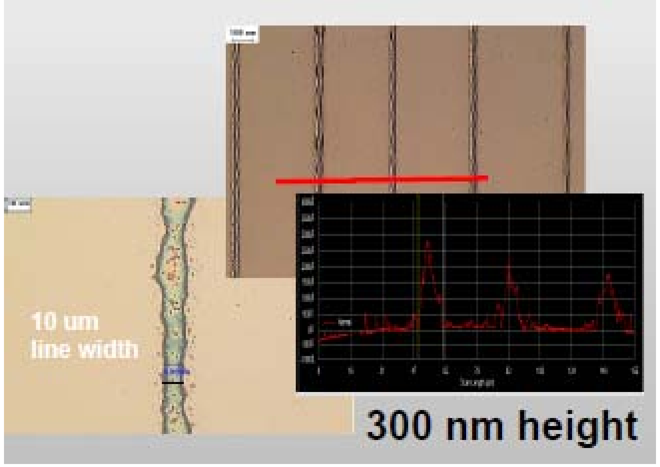


Liquid silane chemistry provides new options for printed silicon







Center for Nanoscale Energy

PV Systems and Module Development:

University Product and Process Development Support

Presenter: Dr. Phil Boudjouk

Organization: North Dakota State University

Contact Info: philip.boudjouk@ndsu.edu

Date: May 26, 2010

This presentation contains no proprietary, confidential or otherwise restricted information

Timeline

- Project start date: July 1, 2008
- Project end date: June 30, 2012
- Percent complete: 31%

Budget: Two Projects

1) PV materials development
2) High value chemicals from bio-based feedstocks

- Total project funding received
  - DOE share: $10.66M
  - Contractor share: $2.67M
- Funding received in FY09: $4.76M
- Funding expected for FY10: $5M

Barriers

- PV Barriers addressed:
  - A. Materials utilization and cost: develop liquid silanes as a low-cost, printable precursor to intrinsic and doped a-Si:H, silicon nitride
  - C. Manufacturing processes: develop new deposition technologies compatible with liquid silane precursors

Partners

- Interactions/ collaborations
  - U-Toledo: liquid silane transformation to a-Si:H
  - UC-Riverside: electrocatalyst development for fuel cells
- Project lead: ND State University
  - Dr. Phil Boudjouk

This presentation contains no proprietary, confidential, or otherwise restricted information

Challenges, Barriers or Problems

This University Product and Process Development Support project seeks to:

- Develop new liquid silane chemistries with applications in new and existing manufacturing schemes; and,
- Optimize deposition processes to take best advantage of liquid silanes in fabricating device heterostructures.

Barriers Addressed

- Materials Utilization and Cost: Improve the synthetic yield of Si_6H_{12}, cyclohexasilane; develop molecular precursors to intrinsic and doped a-Si:H, Si_3N_4; provide samples to industrial PV developers for evaluation; assess production costs; engage chemical manufacturers for synthesis scale-up.
- Manufacturing Processes: Utilize/optimize collimated aerosol beam-direct write, low-pressure and atmospheric-pressure CVD/PE-CVD, and electrospinning processes to deposit thin/patterned films and nanowires from liquid silanes.

Note: this is applied R&D *toward transition* to pilot-scale manufacture

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Objectives for Previous Reporting Period

- Synthetic yield: significantly improve the yield of cyclohexasilane (CHS), an important step in lowering cost of production
  - >70% yield now routinely achieved
- Introduce p- and n-type dopants: modify the chemistry of CHS to enable thin film deposition of intrinsic a-Si:H, doped a-Si:H, Si_3N_4, SiOCN
  - promising CHS derivatives developed
- Demonstrate advantages of CHS in depositing a-Si:H thin films:
  - substantially higher deposition rates achieved by PE-CVD using Si_6H_{12} than lower order silanes
- Demonstrate deposition of patterned a-Si:H using CHS precursor:
  - ~7 µm lines routinely achieved by collimated aerosol beam-direct write (CAB-DW)
  - CAB-DW used to deposit metallic fine-pitch metal current collector lines with pyramidal shape
- Demonstrate conversion of CHS films and lines to a-Si:H and r-Si:
  - a-Si:H and rc-Si produced thermally and by UV irradiation

Supporting EERE Solar Program and DOE R&D Objectives

Wafer-silicon: Heterojunction with Intrinsic Thin Layer (HIT) Cells [Sanyo]

- Minimize grid shadowing; direct-write Ag μ-pyramids (total internal reflection)
- Maximize throughput; high-rate a-Si deposition via CVD of Si_6H_{12}

Film-silicon: MicroMorph a-Si:H/μc-Si:H [Kaneka]

- Manufacturing process integration: atmospheric-pressure printing of Si_6H_{12}
- Deposition of a-Si:H, c-Si, SiOCN (antireflection)
- Atmospheric-pressure PECVD of ZnO:Al

Basic science-related: Emerging Concepts

- Si Cluster Discovery – new physics
  - Laser ablation / time-of-flight mass spectroscopy
  - Solution-phase growth of M@Si_x using Si_6H_{12}-related synthons
- Electrospinning porous a-Si nanowires
- Si nanocrystals and colloids from Si_6H_{12} / -$(SiH_2)_n$- inks
- Inorganic-inorganic heterojunctions

Unique aspects of the CNERM technical approach

- Evaluate Si_6H_{12} as a replacement for SiH_4
  - Higher growth rates with higher-order silanes can reduce bottlenecks
    - PECVD and LPCVD of a-Si:H, µc-Si, Si_3N_4
  - Lower temperature growth with Si_6H_{12} can enable temperature-sensitive substrates

- Evaluate Si_6H_{12} as a liquid precursor to Printed Si
  - Spin coat films to understand stresses during transformation from polymer to a-Si:H
    - What is the upper thickness limit for uncracked spun coated films?
  - Electrospinning 100 to 2000 nm diameter porous a-Si:H wires

- Develop Si_6H_{12} and derivatives as molecular precursors to intrinsic and doped a-Si:H and Si_3N_4 thin films and patterned structures
  - Atomically distribute n- and p-type dopants by attaching P- and/or B-containing chemical functionalities to the Si_6H_{12} ring prior to ring-opening polymerization
  - Formulate a single-source precursor that yields Si_3N_4 (with good H-levels) after thermoloysis
  - 7 µm-wide printed silicon lines using collimated aerosol beam direct-write (CAB-DW)

- Evaluate atmospheric-pressure PECVD in Si solar cell structures
  - Deposit ZnO:Al transparent conductors using solid-source precursors
  - Deposit SiOCN anti-reflection coatings using commercial sources and Si_6H_{12}

Approach

PV Barriers Addressed

- Materials utilization and cost
  - Evaluate processing advantages of CHS versus production costs
- Manufacturing processes
  - Develop thin film and printed line deposition technologies
  - Emphasize atmospheric-pressure and low temperature methods that take advantage of Si_6H_{12} properties

Integration with Program

- NREL informal interaction
  - Partially competed cells obtained from NREL to test printed grid electrode approach for HIT cells
- U-Toledo
  - Thin film spectroscopic ellipsometry studies, transparent SWNT films, carrier dynamics analyses
- Commercial PV developers
- Chemical manufacturers

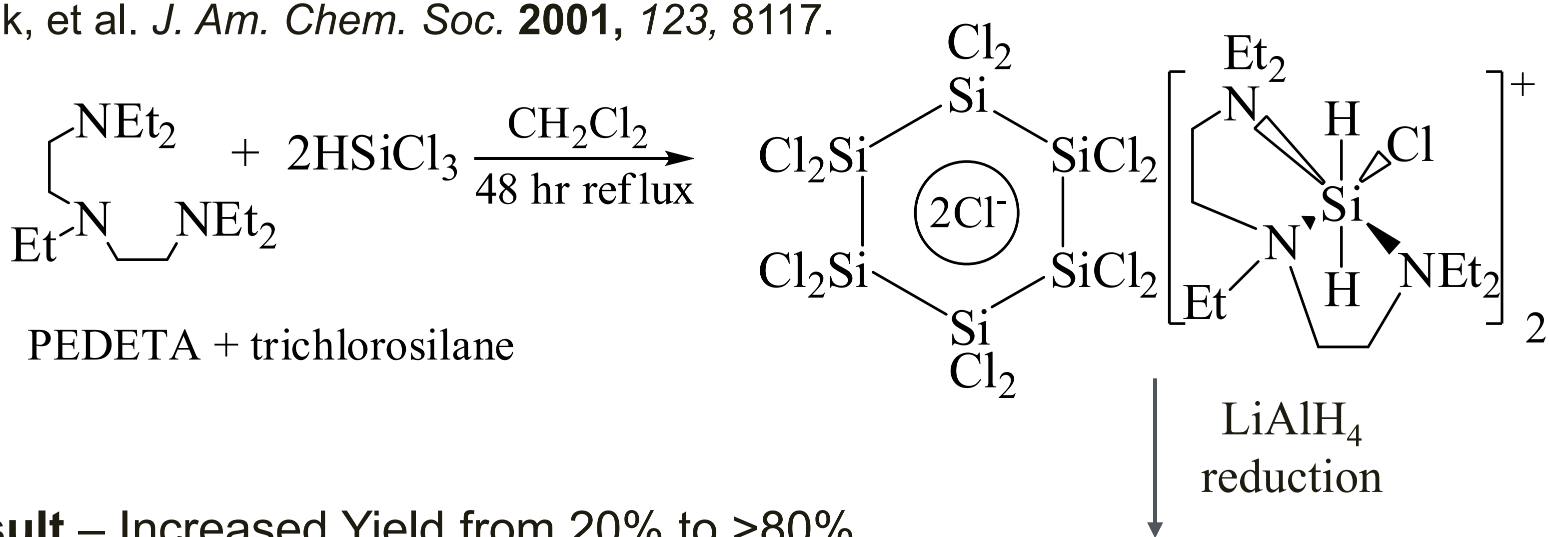
Key milestones and go/no-go decisions

- Develop CHS derivatives that can be converted into n- and p-type thin films
- Fabricate heterojunction solar cell by PECVD with CHS precursors
- Demonstrate heterojunction solar cell that uses APPECVD to grow the intrinsic layer
- Deposit quality silicon nitride antireflection layers using Si_6H_{12} in PECVD

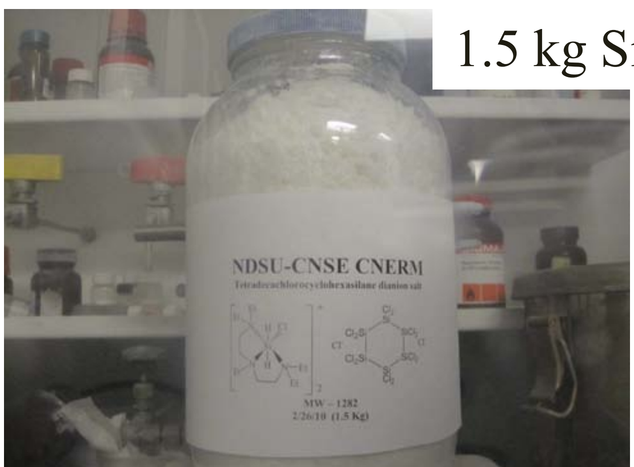
Cyclohexasilane Si_6H_{12} Chemistry

Amine-promoted disproportionation and redistribution: Si-Si bond formation

P. Boudjouk, et al. *J. Am. Chem. Soc.* **2001**, *123*, 8117.

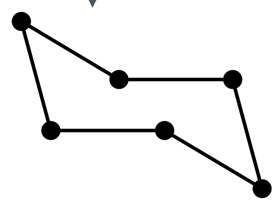


2009 Result – Increased Yield from 20% to >80%



1.5 kg $Si_6Cl_{14}^{2-}$ salt

~ 150 g Si_6CH_{12} (l)



$\equiv$ Si_6H_{12}

bp. ~ 220 °C
(80 ° C/10 mTorr)
mp. 18 °C
ρ 0.97 g/mL

Realistic cost target $100/kg as per chemical manufacturer

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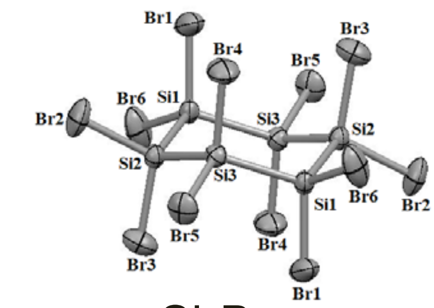
Adduct Chemistry of Si_6X_{12} (X= Cl,Br)

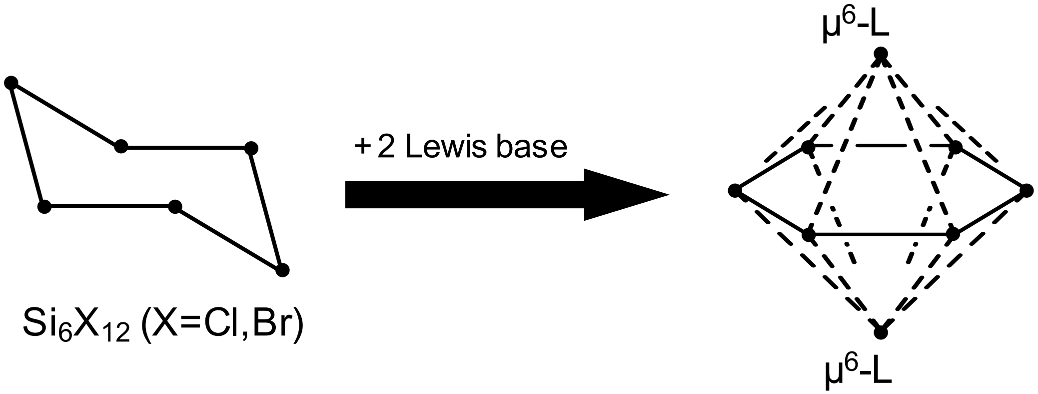
Molecular Halogenation of Si_6H_{12}

[redacted]

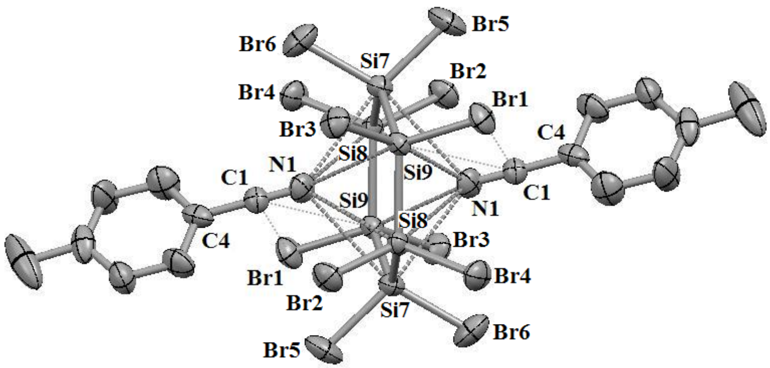


Si_6Br_{12}

Lewis Acid-Base Adducts of Si_6X_{12}



Si_6X_{12} (X=Cl,Br)



Si_6Br_{12}.2 p-tolunitrile

"New Landscape in Si Chemistry" forms basis of a route to Si6-based molecular wires

Boudjouk, P. et al., "Inverse Sandwich" Complexes of Perhalogenated Cyclohexasilane, *Organometallics*, **2010**, **DOI:** 10.1021/om1000716

Accomplishments / Progress / Results
Si_6H_{12} Precursor to Si-based Materials

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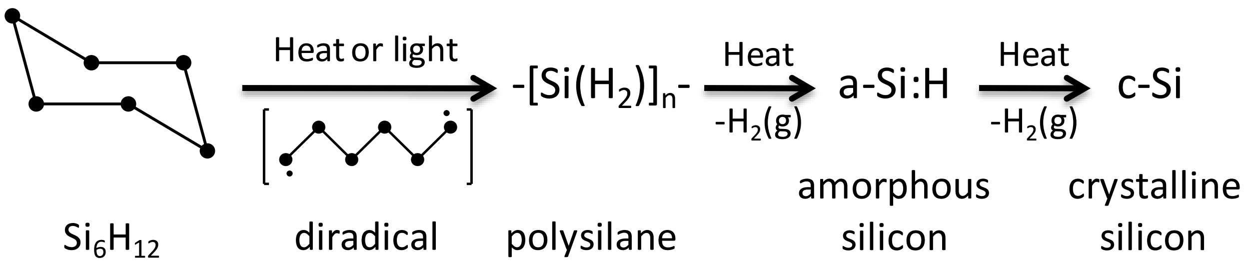
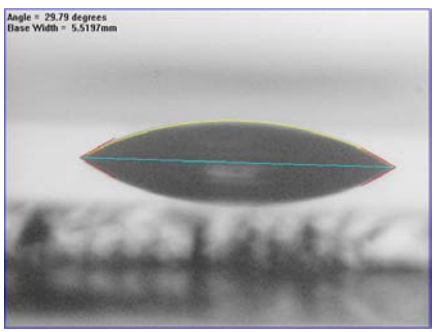
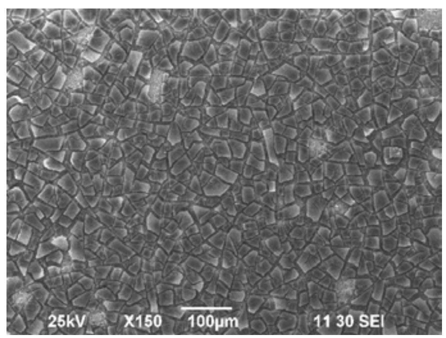


Typical Ink Formulation

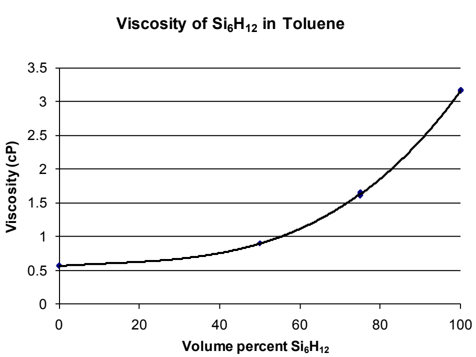
$-[Si(H_2)]_n-$ & Si_6H_{12} in toluene

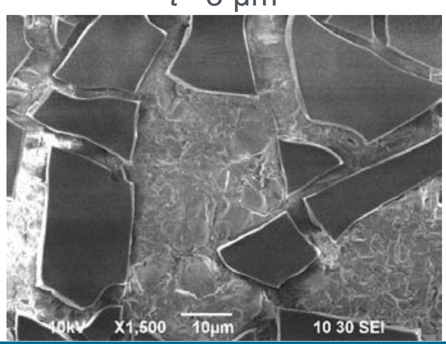
Spin Coating - Thicker Films (t > 500nm) Crack





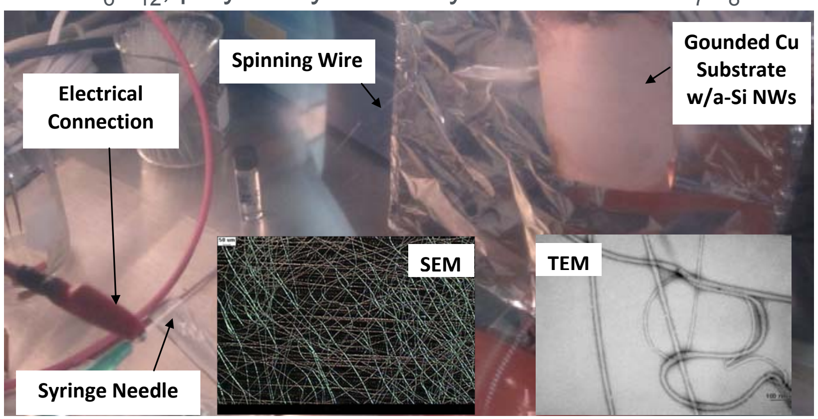
t ~3 µm

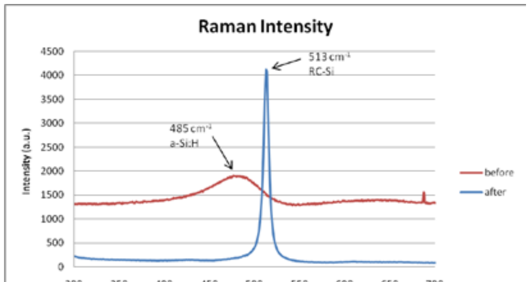




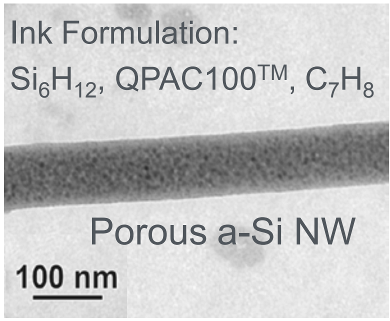
Electrospinning Addresses Shrinkage

Si_6H_{12}, polymethylmethacrylate in toluene C_7H_8





[Note: Raman laser rc-Si]



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Doping Printed Silicon

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Ring-Appended Dopants (covalent Si-P bond)

Si_6H_{12} + $HgCl_2$ → $Si_6H_{11}Cl$ (60%)

Intl. Symp. OrganoSilicon XV-Jeju 06/02/2008

$Si_6H_{11}Cl$ + KPH_2 or $LiAl(PH_2)_4$ or $^iBu_2AlPH_2$ —✕→ $Si_6H_{11}PH_2$

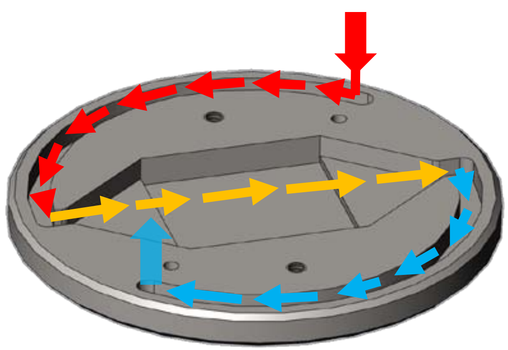
→ $-(Si(H_2))_n-$ polydihydrosilane

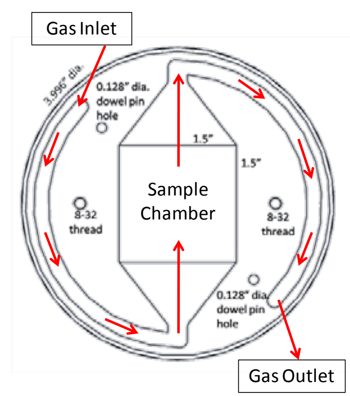
April 2008 – March 2010

Gaseous Ex-situ Dopants Diffusion of B (or P) in Polyhydrosilane Films

Jan 2010 to present

1. Low-Temp "Polydihydrosilane" Film Deposition
   a. Spin-coating, CAB-DW or low-temperature PECVD/CVD/APPE-CVD
2. Thermal Treatment at 80 to 450 °C with Flowing Hydride (B_2H_6 or PH_3)





<u>Activation Energy of B</u>

Si ~3.8 eV

a-Si ~3.0 eV

$-(SiH_2)_n-$ not established

Other Dopant Results: remain confidential

Accomplishments / Progress / Results
Si_6H_{12} precursor in PECVD

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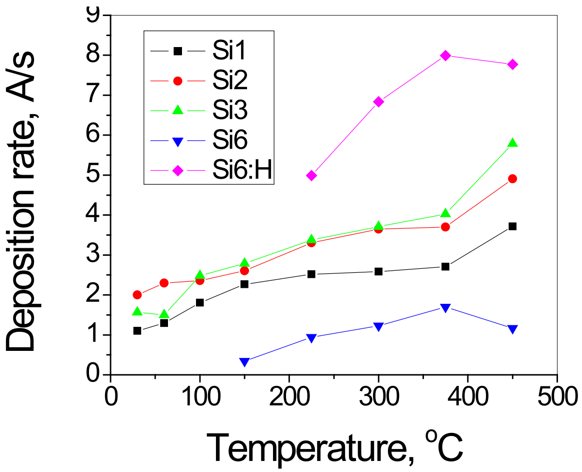
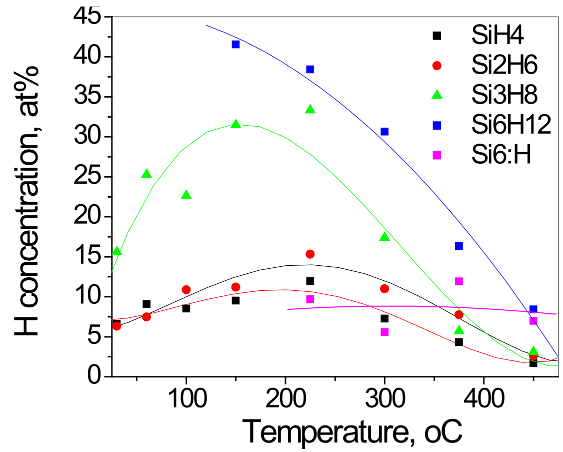
Amorphous Si: P_{dep} = 1 Torr; Ar plasma power = 94 mW/cm^2 @ 13.56 MHz.

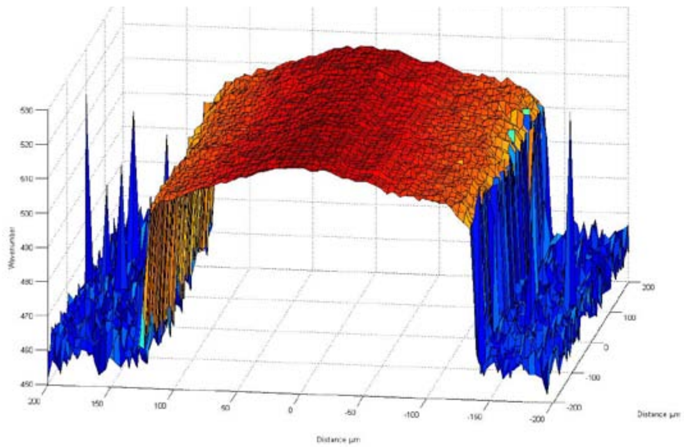
PECVD a-Si Deposition Rates



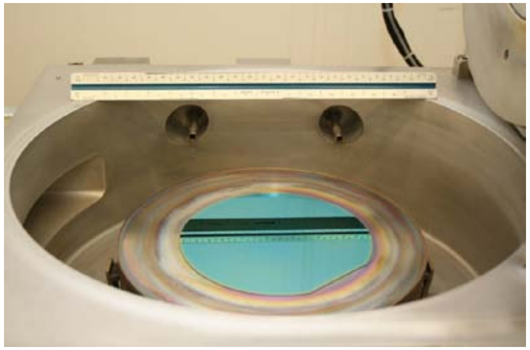
H_2 Content in PECVD Films



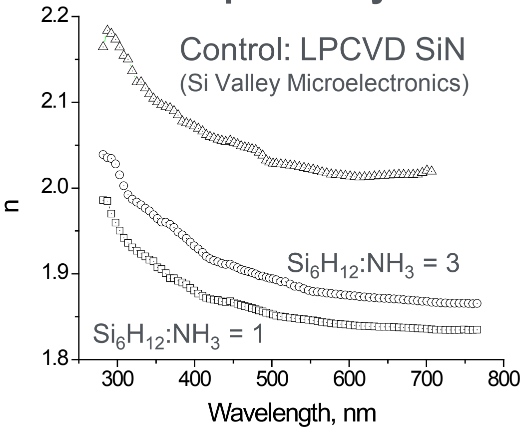
Raman Map of Laser Crystallized Si



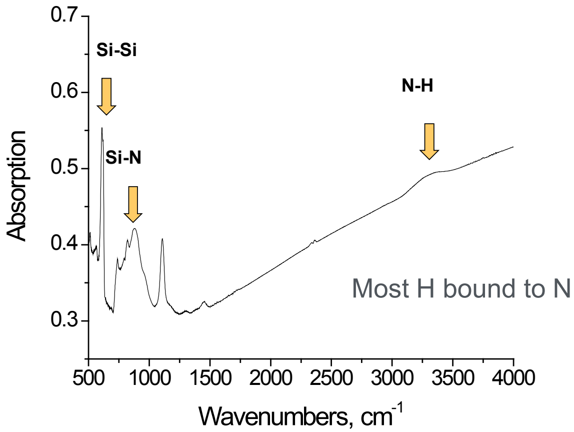
Si Nitride: Si_6H_{12} + NH_3; P_{dep} = 0.7 Torr; N_2 Plasma density= .028 mW/cm^2 @13.56 MHz.



Ellipsometry



FTIR



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Accomplishments / Progress / Results
PECVD at 760 Torr

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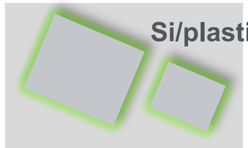
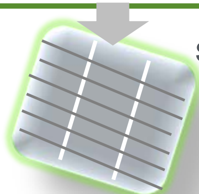
Single Crystalline Si PV Process

Plug-In Process



Potential Atmospheric Pressure PECVD Processes

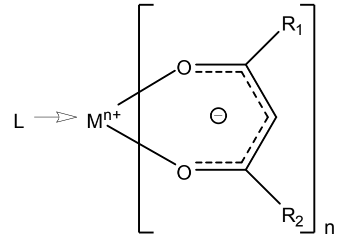
- Saw damage etch & texturing
- *p-i-n* layer deposition* ←
- *removal of front-rear side short*
- *removal of phosphorous glass*
- *antireflection coating* ←
- *Contacting /TCO* ←
- *Sintering*



>90% of market

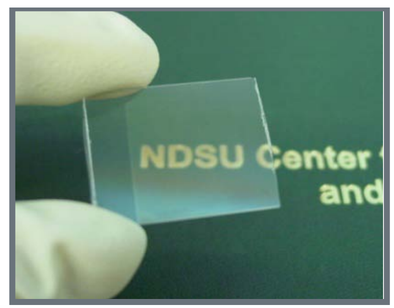
Adapted after
Dani, et al., *Contrib. Plasm. Phys.* **2009**, *49*, 662.

Precursors



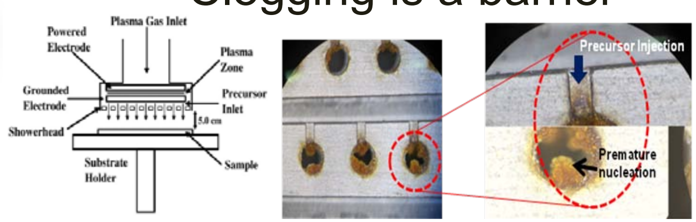
In-Sn-O

85 %T; ρ~7 mΩ.cm

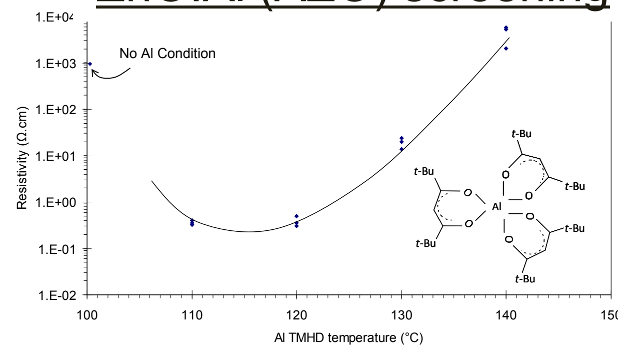


Surfx™ 250 D Head

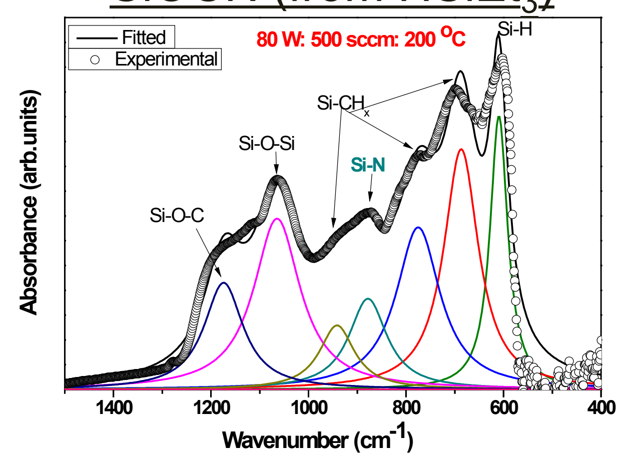
Clogging is a barrier



ZnO:Al (AZO) screening



SiOCN (from $HSiEt_3$)



n = 1.43-1.54
H = 2 to 5 GPa
E_r = 40 to110 GPa

Accomplishments / Progress / Results
Aerosol Printed Back Contacts - Ag

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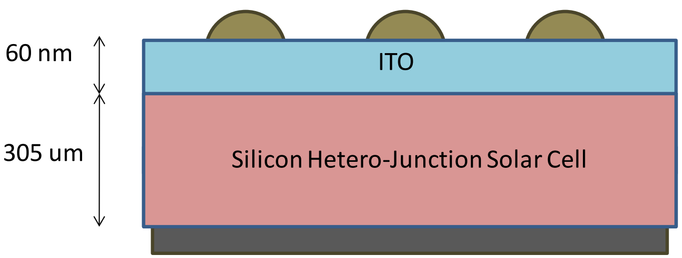
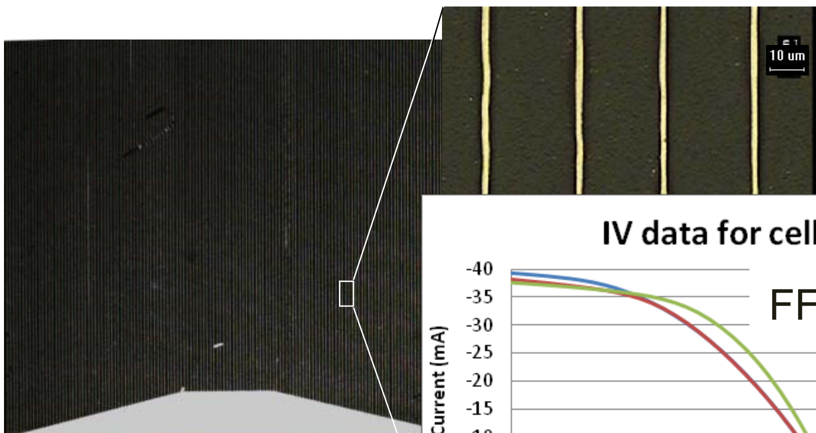
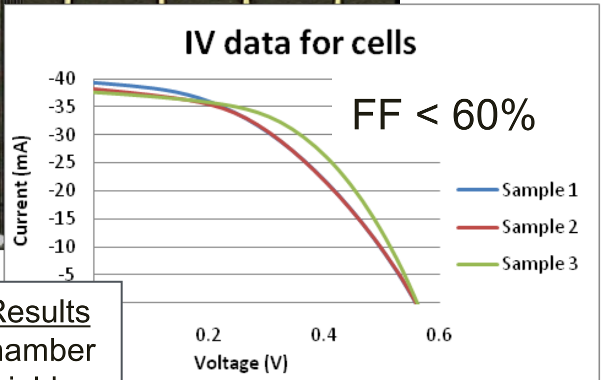
Prototype HIT Test Structure*



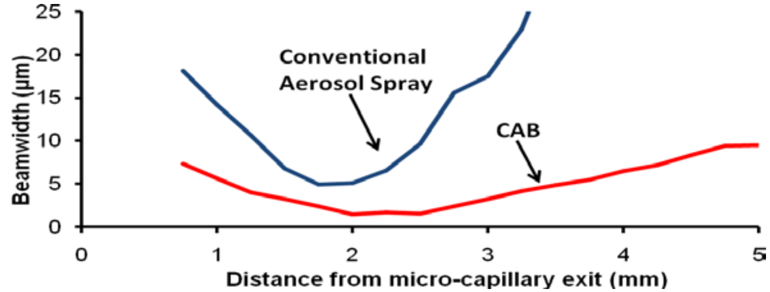




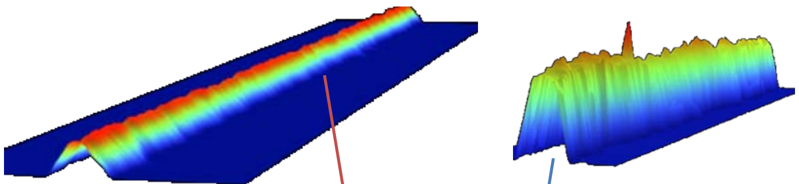
Promising Initial Results
NREL multiuse chamber being cleaned to yield higher fill factor devices

*Uncontacted Cells Courtesy Eugene Iwaniczko, Matt Page and Qi Wang

NDSU's Three-Nozzle CAB-DW™

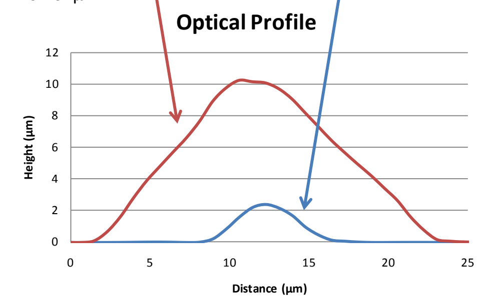


Geometry: Total Internal Reflection



Average Height: 9.62µm
Average Width: 29.09µm
Average Area: 102.67µm²

Average Height: 2.52µm
Average Width: 8.398µm
Average Area: 10.07µm²



Aerosol Printed Back Contacts - Si

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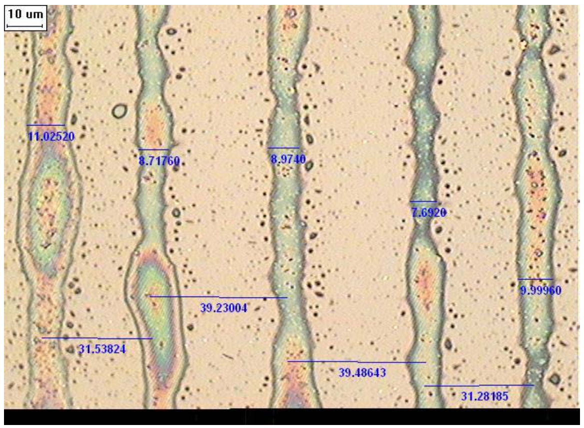
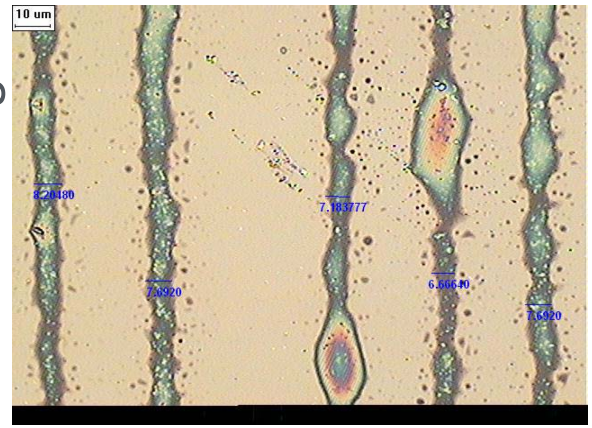
Optical Micrographs of Printed Silicon via CAB-DW Of Si_6H_{12}-based Ink

After UV

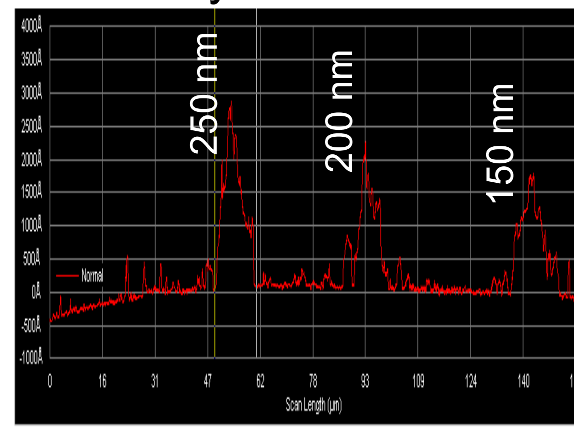


50 X mag

After UV + 350 °C



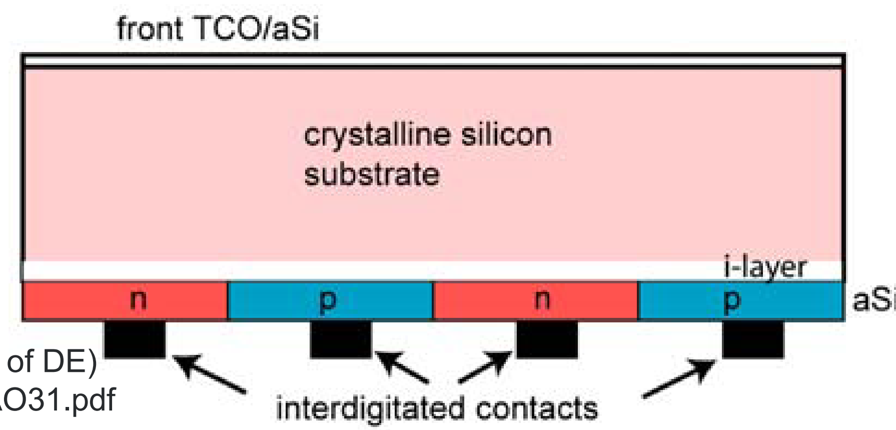
Stylus Profile



Previous Studies: Limited to T < 400 °C; Focused Mainly on Low-Temperature Dopants

<u>Potential Technology Pathway Partnership</u>

Printed Si interdigitated back contact silicon heterojunction solar cells



From Birkmire et al. (Inst. Energy Conversion @ University of DE)
http://www.udel.edu/iec/Publications/22nd_EU_PVSEC_2AO31.pdf

Future Plans (FY 2011 and beyond)

- Improve the synthetic yield of Si_6H_{12} toward 90%.
- Develop molecular precursors to intrinsic and doped a-Si:H as well as Si_3N_4.
- Provide samples to industrial PV developers for evaluation.
- Assess production costs; engage chemical manufacturers for synthesis scale-up.
- Gain a refined understanding of Si_6H_{12}-based inks formulation toward reproducibility.
- Determine relevance of porous amorphous silicon nanowires.
- Investigate the formation of germanium-containing spherical silicon.
- Determine if printed silicon lines are candidate absorbers for microconcentrator PV.
- Consider a 500 MW/yr PV manufacturing strategy plant that employs NDSU technologies as enabling steps in a wafer-Si plant to be setup in ND's Cass county in the 2017 timeframe.

Collaborations

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

- University of Toledo – Subawardee FY 09-10
  - Mike Heben, Randy Ellingson and Rob Collins (Wright Center for PV Innovation and Commercialization)

  THEMES AND STATUS

  Ellipsometry of polysilane to a-Si:H transition, Liquid silanes + SWNT films, carrier lifetimes
    - Si_6H_{12}-derived a-Si:H (NDSU) and SWNT (UT) thin film samples exchanged
    - Initial PL of liquid silane-derived film consistent with the literature

  EXTENT OF INTERACTION
  - Semi-annual site visits, weekly conference call
- Iowa State University – Subawardee FY11
  - Sam Houk, Javier Vela and Vik Dalal

  THEMES AND STATUS

  Laser Ablation TOF-MS for Cluster Discovery, Low-bandgap Pb NCs, a-Si:H Film Development
    - Subaward included in the FY11 Submission to DoE by NDSU
    - Formal (Houk, Vela) and informal (Dalal) exchanges envisioned

Business Development

- Fine Chemical Manufacturers – targeting a partner for Si_6H_{12} production
  - Ongoing discussions with several producers; one active collaboration at the moment
  - Ongoing discussions with printed silicon PV "end-users"; one active collaboration

Mandatory Summary Slide

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- The NDSU Center for Nanoscale Energy is a University P&P with several new technologies that are being validated
- NDSU CNERM has been proactive in pursuing relationships with industry, university and national labs to facilitate the pace of development; developing a niche within the PV innovation pipeline
- Research progress:
  - Significantly improved the synthetic yield of CHS, critical in lowering the cost of production
  - Demonstrated substantially higher silicon deposition rates using PE-CVD and CHS precursors than achievable with lower order silanes
  - Discovered unusually high Lewis acidity at sites within the CHS ring, responsible for formation of unique adducts
  - Collimated aerosol beam-direct write technology enables ~7 micron lines of a-Si:H to be written routinely. Technology enables fine-pitch metal current collector lines to be deposited with a pyramidal shape
  - Conversion of CHS films and lines to a-Si:H and rc-Si demonstrated
- Key milestones:
  - Optimize methods to introduce dopants at targeted levels into CHS, to be utilized in preparing silicon thin films and lines
  - Demonstrate deposition of silicon nitride antireflection coatings at atmospheric pressure using CHS precursors
  - Create heterojunction solar cells utilizing CHS precursors