Liquid silane chemistry provides new options for printed silicon
Overview

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
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 \( \text{Si}_6\text{H}_{12} \), cyclohexasilane; develop molecular precursors to intrinsic and doped a-Si:H, \( \text{Si}_3\text{N}_4 \); 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
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, Si₃N₄, 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 Si₆H₁₂ 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$_6$H$_{12}$

**Film-silicon: MicroMorph a-Si:H/µc-Si:H [Kaneka]**
- Manufacturing process integration: atmospheric-pressure printing of Si$_6$H$_{12}$
- 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$_6$H$_{12}$-related synthons
- Electrospinning porous a-Si nanowires
- Si nanocrystals and colloids from Si$_6$H$_{12}$ / -(SiH$_2$)$_n$- inks
- Inorganic-inorganic heterojunctions
Unique aspects of the CNERM technical approach

• Evaluate Si$_6$H$_{12}$ 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$_3$N$_4$
  – Lower temperature growth with Si$_6$H$_{12}$ can enable temperature-sensitive substrates

• Evaluate Si$_6$H$_{12}$ 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$_6$H$_{12}$ and derivatives as molecular precursors to intrinsic and doped a-Si:H and Si$_3$N$_4$ thin films and patterned structures
  – Atomically distribute n- and p-type dopants by attaching P- and/or B-containing chemical functionalities to the Si$_6$H$_{12}$ ring prior to ring-opening polymerization
  – Formulate a single-source precursor that yields Si$_3$N$_4$ (with good H-levels) after thermolysis
  – 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$_6$H$_{12}$
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
Accomplishments / Progress / Results  
Cyclohexasilane Si$_6$H$_{12}$ Chemistry

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


\[
\text{Et}_2\text{N} + 2\text{HSiCl}_3 \xrightarrow{48 \text{ hr reflux}} \text{CH}_2\text{Cl}_2 \rightarrow \text{PEDETA} + \text{trichlorosilane}
\]

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

- 1.5 kg Si$_6$Cl$_{14}^{2-}$ salt
- ~ 150 g Si$_6$CH$_{12}$ (l)

Realistic cost target $100/kg as per chemical manufacturer

bp. ~ 220 °C  
(80 °C/10 mTorr)  
mp. 18 °C  
$\rho$ 0.97 g/mL
Molecular Halogenation of $\text{Si}_6\text{H}_{12}$

$\text{Si}_6\text{H}_{12}$ reacts with $\text{X}_2$ in the presence of $\text{CH}_2\text{Cl}_2$ to form $\text{Si}_6\text{X}_{12}$ (X=Cl,Br) at $\sim -80$ to $-90 \, ^\circ\text{C}$.

Lewis Acid-Base Adducts of $\text{Si}_6\text{X}_{12}$

$\text{Si}_6\text{X}_{12}$ (X=Cl,Br) forms Lewis acid-base adducts with $\mu^6$-L bonding.

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

Accomplishments / Progress / Results

Si$_6$H$_{12}$ Precursor to Si-based Materials

**Typical Ink Formulation**

-\([Si(H_2)]_n\) - & Si$_6$H$_{12}$ in toluene

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

**Electrospinning Addresses Shrinkage**

Si$_6$H$_{12}$, polymethylmethacrylate in toluene C$_7$H$_8$

[Note: Raman laser rc-Si]
Accomplishments / Progress / Results  
Doping Printed Silicon

Ring-Appended Dopants (covalent Si-P bond)

\[
\text{Si}_6\text{H}_{12} + \text{HgCl}_2 \rightarrow \text{Si}_6\text{H}_{11}\text{Cl} \ (60\%) \\
\text{Si}_6\text{H}_{11}\text{Cl} + \text{KPH}_2 \quad \text{or} \quad \text{LiAl(PH}_2)_4 \quad \text{or} \quad \text{iBu}_2\text{AlPH}_2 \\
\rightarrow -\left(\text{Si(H}_2\right)_n- \text{ polydihydrosilane}
\]

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

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\text{2H}_6 or PH\text{3})

Other Dopant Results: remain confidential

Activation Energy of B
Si  ~3.8 eV  
a-Si  ~3.0 eV
-(SiH\text{2})_n- not established
Accomplishments / Progress / Results

Si$_6$H$_{12}$ precursor in PECVD

**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**

**Si Nitride:** $Si_6H_{12} + NH_3; P_{dep} = 0.7$ Torr; $N_2$, Plasma density = 0.028 mW/cm$^2$ @ 13.56 MHz.

**Ellipsometry**

**FTIR**

Most H bound to N
Accomplishments / Progress / Results
PECVD at 760 Torr

Single Crystalline Si PV Process

**Plug-In Process**

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

Solar cell

>90% of market

**Precursors**

In-Sn-O

85 %T; ρ~7 mΩ.cm

**ZnO:Al (AZO) screening**

**SiOCN (from HSiEt₃)**

Surfx™ 250 D Head

Clogging is a barrier

Adapted after
Accomplishments / Progress / Results
Aerosol Printed Back Contacts - Ag

Prototype HIT Test Structure*

NDSU’s Three-Nozzle CAB-DW™

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

*Uncontacted Cells Courtesy Eugene Iwaniczko, Matt Page and Qi Wang
Accomplishments / Progress / Results
Aerosol Printed Back Contacts - Si

Optical Micrographs of Printed Silicon via CAB-DW Of Si$_6$H$_{12}$-based Ink

After UV

After UV + 350 °C

Stylus Profile

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

Potential Technology Pathway Partnership
Printed Si interdigitated back contact silicon heterojunction solar cells

From Birkmire et al. (Inst. Energy Conversion @ University of DE)
http://www.udel.edu/iee/Publications/22nd_EU_PVSEC_2AO31.pdf
Future Plans (FY 2011 and beyond)

- Improve the synthetic yield of Si$_6$H$_{12}$ toward 90%.
- Develop molecular precursors to intrinsic and doped a-Si:H as well as Si$_3$N$_4$.
- Provide samples to industrial PV developers for evaluation.
- Assess production costs; engage chemical manufacturers for synthesis scale-up.
- Gain a refined understanding of Si$_6$H$_{12}$-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

- **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$_6$H$_{12}$-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$_6$H$_{12}$ production**
  - Ongoing discussions with several producers; one active collaboration at the moment
  - Ongoing discussions with printed silicon PV “end-users”; one active collaboration
• 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
Supplemental Slides
Project Schedule

1. Initiation Date: July 01, 2008
2. Original Expected Completion Date: June 30, 2012
3. Current Expected Completion Date: June 30, 2012
4. Reasons for Delay: not applicable

Technical Milestones and go/no-go’s for FY09 and FY10

Demonstrate four different types of functionalized Si$_6$H$_{12}$ with Si-heteroatom bonds.

Realistic assessment indicating that Si$_6$H$_{12}$-derived films can be more cost-effective to conventional CVD and PECVD a-Si film precursors.

Form a crack-free a-Si:H film two µm in thickness from a printed Si$_6$H$_{12}$-based ink.

Demonstrate a metal silicide/a-Si:H junction using a low-T solution approach.

Grow transparent conductors w/ $R_{\text{sheet}}$ < 100 Ω/square by atmospheric-pressure PECVD.

Grow antireflection coatings w/ T > 85% (300-1200 nm) under various incident angles.

Demonstrate an 8% HIT solar cell where Si$_6$H$_{12}$ is the precursor to intrinsic a-S:H layer.
Budget Center for Nanoscale Energy

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- Current project was planned for a four year period of performance (July 01, 2008-June 30, 2012)
- Project spending is less than anticipated (31% actual versus 44% elapsed time), due to delayed project initiation – especially catalysis project
Responses to Previous Year Reviewers’ Comments

- **Criterion 1.** Relevance to overall DOE objectives - relevance to PV questioned. Focus of PV project on barriers of materials utilization/cost and manufacturing processes. New liquid silane chemistry is being developed that provides new options for silicon deposition.

- **Criterion 2.** Approach to performing the R&D – noted that resources at NDSU are considerable; research not focused on PV technical barriers; cost of proposed manufacturing processes not assessed. PV project directed towards identified technical barriers of materials utilization/cost and manufacturing processes. Significant gains made in synthetic yield of liquid silanes. Industrial partner engaged to evaluate scale-up, and likely production costs established. Use of liquid silane in PECVD deposition led to higher deposition rates and greater precursor utilization.

- **Criterion 3.** Technical accomplishments and progress toward overall project and DOE goals – noted that project had recently started; difficult to assess technical progress; direction of research too broad. Context of research highlights more directly tied to PV goals and critical barriers. Technical direction of PV project narrowed, as described.

- **Criterion 4.** Collaborations with other institutions – University of California-Riverside and University of Toledo seen as strong partners. Collaborations with NREL continue. Interactions with Ames Lab in deposition of silicon thin films and Si clusters established. Liquid silane or dianion salt provided to commercial PV developers and chemical manufacturers for evaluation.

- **Criterion 5.** Proposed future research – plans do not adequately address critical barriers for PV. Future research activities will address scale-up of cyclohexasilane synthesis, development of doped molecular precursors, deposition of intrinsic and doped silicon thin films, patterned silicon, deposition of silicon nitride antireflection coatings, electrical and optical property characterization.


**PATENTS**


Oxidative Catalysis

Development of polymers from precursors derived from renewables, using combinatorial methods
Challenges, Barriers or Problems
Oxidative Catalysis

- Identify low-cost, efficient, scalable catalytic routes to extract high value chemicals from renewable sources such as oil seeds, focusing on precursors to polymers including long-chain dicarboxylic acids.
- Catalytic process intended to replace ozonolysis, a low-efficiency, energy-intensive, high risk, and costly technology.
- Targeted products include nyons, polyesters, waxes, and surfactants, having properties superior to those readily synthesized from petrochemicals. An example is nyons having substantially lowered moisture absorption tendencies.
- Optimization of the catalyst to convert oil seeds to useful dicarboxylic acids is a multivariant problem that requires extensive experimentation.
- Optimization of polymers and co-polymers also is a multivariant problem requiring formulation and property evaluation of a very large number of materials.
Approach  
Oxidative Catalysis

- Derive long-chain dicarboxylic acids from oil seeds and cellulosics by selective oxidation
- Optimize tungsten oxide-based and other novel catalysts developed at NDSU by combinatorial methods as a means of accelerating development
- Formulate families of polymers and co-polymers derived from renewable resources, and evaluate physical, mechanical, and chemical properties. Use combinatorial methods to accelerate the pace of development

Erucic acid conversion to brassylic and nonanoic acids by selective oxidation

General structure of co-polyamides of interest
• Achieve >50% yield of long-chain dicarboxylic acids from plant-derived mono-olefins on a 100 gram scale (June 2010, milestone achieved).
• Achieve >50% yield of furan dicarboxylic acids from sugars by selective catalytic oxidation (June 2010, milestone achieved).
• Complete optimization of tungsten oxide-based and other novel catalysts developed at NDSU by combinatorial methods (September 2010).
• Develop flow sheets to optimize yields of dicarboxylic acids of model seed oils containing multiple fatty acids (June 2011).
• Formulate families of polymers and co-polymers derived from renewable resources, and evaluate physical, mechanical, and chemical properties. Use combinatorial methods to accelerate the pace of development (June 2011).
• A No-Go Decision Point (June 2011) would be reached if plant-derived polymers do not show high potential for replacing petroleum-derived polymers (reduced swelling, lower price, equal or greater strength).
Influence of Solvent and Oxygen on Reaction Efficiency:
Yields enhanced with elimination of organic solvent, presence of phase transfer catalyst

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### Solvent Screening: consistently higher yields with t-butanol

#### Entry Catalyst Solvent Reaction Time Yield (%)

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**Phase Transfer Catalysts:**

Bu$_4$NHSO$_4$ most effective

| Entry | Catalyst | Additive | Reaction Time (h) | Yield (%)
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Selective Oxidation of Oleic Acid: Catalytic processes developed for oxidative cleavage of erucic acid directly applicable to this important fatty acid from oil seeds and other sources.

Oleic Acid

\[
\text{Oleic Acid} \xrightarrow{\text{cat. (0.1 eq)}} \text{Additive (0.1 eq)} \xrightarrow{\text{H}_2\text{O}_2 (6.0 eq)} \xrightarrow{\text{O}_2 (1 \text{ atm})} \xrightarrow{\text{Solvent}} \xrightarrow{85 \degree \text{C}, 24 \text{ h}} \text{Nonanoic Acid} + \text{Nonanedioic Acid}
\]

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<td>NO</td>
<td>Bu\text{4NHSO}_4</td>
<td>82%</td>
</tr>
<tr>
<td>10x</td>
<td>1 atm</td>
<td>NO</td>
<td>Bu\text{4NHSO}_4</td>
<td>85%</td>
</tr>
</tbody>
</table>
Accomplishments / Progress
Oxidative Catalysis

Melting temperatures for copolymers derived from adipamide and terephthalamide (TA) repeat units

- Melting temperatures of series comparable to nylon 6 (220°C) and nylon 6,6 (260°C)
- No information available on properties including crystallization rate, glass transition temperature, melt rheology, moisture adsorption, mechanical properties for series
Melting and glass transition temperatures for terephthalamide/adipamide copolymers. Glass transition temperatures are considerably higher than found fornylons, expected to correlate with improved moisture resistance.

**Oxidative Catalysis**

**Melting Temperature**

**Glass Transition Temperature**
Terephthalamide/adipamide copolymer compositions exhibit favorable properties for injection molding (small difference between melting and crystallization temperatures)
• The purpose of this project is to develop plant-derived polymers with high potential for replacing petroleum-derived polymers. Important considerations include reduced swelling, lower price, equal or greater strength, and improved processability. Polymer precursors and other high value chemicals are derived by selective oxidation of renewable resources including oil seeds and cellulosics. High throughput combinatorial methods were applied to optimize oxidative catalysis as well as to formulate polymer families.

• Long chain dicarboxylic acids have been derived in >80% yields from fatty acids found in oil seeds by selective oxidative cleavage using tungsten-based and other catalysts.

• Furan dicarboxylic acids have been synthesized in high yields by selective catalytic oxidation of cellulosic materials. This product is a precursor to a new class of polyamide polymers.

• A series terephthalamide/adipamide copolymers have been prepared from long-chain dicarboxylic acids derived from renewable feedstocks. Compositions have been identified that exhibit significant processing advantages over commercial nylons.
• University of California-Riverside (Prof. Robert Haddon, PI) – subcontract, developing electrocatalysts for oxygen reduction
Future Plans (FY 2011 and beyond)
Oxidative Catalysis

- Using combinatorial methods, optimize catalytic processing parameters to achieve maximum yields of long-chain dicarboxylic acids from renewable resources at a lower cost than possible from petroleum.
- Demonstrate dicarboxylic acid synthesis at >2 liter scale. Develop flow sheets to optimize yields of diacids from model seed oils containing multiple fatty acids.
- Achieve >80% yield of furan dicarboxylic acid (FDCA) and 2-ethyl 1-hexene (2E1H) from catalyzed reactions of cellulosics.
- Establish structure/property relationships for polyamides from long-chain dicarboxylic acids.
- Establish structure/property relationships for polyamide polymers from FDCA and carbocationic polymers derived from 2E1H.
- Go/No Go Decision Point: Demonstrate that plant-derived polymers show high potential for replacing petroleum-derived polymers, considering properties such as reduced swelling, lower price, processability, and equal or greater strength.