1. Market outlook

2. A Suite of projects
   a) Metallurgical Silicon MGSi
   b) *(The Silgrain Process UMG)*
   c) Solargrade Silicon SoG
   d) Silicon wafers

3. Conclusions

<table>
<thead>
<tr>
<th>16kWp</th>
<th>$ 53,894</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total system cost</td>
<td>$ 53,894</td>
</tr>
<tr>
<td>Federal tax credit</td>
<td>$ 16,168</td>
</tr>
<tr>
<td>PA (SEP)</td>
<td>$ 7,500</td>
</tr>
<tr>
<td>PA SREC</td>
<td>$ 8,847</td>
</tr>
<tr>
<td><strong>Net Cost to Rob</strong></td>
<td><strong>$ 21,379</strong></td>
</tr>
</tbody>
</table>

Pay back about 5 years with Pittsburgh conditions
The Market Outlook

- 1976: 72 $/Wp

- Silicon shortage

- 2011: 0.92 $/Wp

- First Solar Thin Film

- Module price 2011 $/Wp

- Installed GWp

- SOG-Si 20%
- Installation 30%
- Ingot/Wafer 28%
- Module 9%
- Cell Manufacture 13%

Growth of PV Industry

- Centralized on grid
- Decentralized on grid
- Non domestic off grid
- Domestic off grid

Source: Paul Maycock, Bloomberg New Energy Finance
Metallurgical Silicon Production → Poly-Crystalline Silicon Production → Silicon Wafers → Solar Cells → Solar Modules

Figure 5.3: The lining, tapping area and electrode system. The additional equipment for raw material supply, bus bar system and water cooled parts will increase the complexity of the presentation of a large furnace. With courtesy to Elkem Carbon.

SiO₂ + 2 C = Si + 2 CO

energy

Micro-electronics
Photovoltaics
Aluminum
Silicones

Maximum October 2008 @ $2.74 per kg
Control and Optimization of Silicon (COPS)

M. Ruszkowski, J. H. Hill, N. Arora (L. Biegler) ELKEM.

Figure 5.3
The lining, tapping area and electrode system. The additional equipment for raw material supply, bus bar system and water cooled parts will increase the complexity of the presentation of a large furnace. With courtesy to Elkem Carbon.

\[ \text{SiO}_2 + 2 \text{ C} = \text{Si} + 2 \text{ CO} \]

SiO₂ + 2 C = Si + 2 CO

energy

Micro-electronics
Photovoltaics
Aluminum
Silicones
## Control and Optimization of Silicon (COPS)

*M. Ruszkowski, J. H. Hill, N. Arora (L. Biegler) ELKEM.*

### Process Modeling, parameter and State Estimation, Control, Optimization

**DAE System**
- Set of ODEs in $t$
- Set of AEs
- AE at boundaries
- Set of AEs

**DAE System Solver**
- DASPK 3.0

### Solution: Dynamic spatial profiles

\[
\frac{\partial z}{\partial t} + \frac{\partial v_z}{\partial x} = D \frac{\partial^2 z}{\partial x^2} + \sigma + \text{ODE's and constraints}
\]

**PDAE System**
- PDEs in $t$ and $z$
- PDEs in $z$
- BCs
- AE constraints

### Collect data

- Measure Si-Production
- SiO in off gas

**Manipulate**
- C, SiO2 feed

**Electrical Power**

\begin{align*}
&\text{C source mix: } C_{(s)} \\
&\text{Quartz: } \text{SiO}_{2(s)}
\end{align*}

\begin{align*}
&\text{CO}_{2(g)} \\
&\text{SiO}_{2(g)}
\end{align*}

\begin{align*}
&\text{C, SiO}_2
\end{align*}

\begin{align*}
&\text{SiC}_{(s)} + \text{SiO} \rightarrow \text{Si}_1 + \text{CO}_{(g)} \\
&\text{ii}_R: 2\text{SiO}_{(g)} \rightarrow \text{Si}_{(l)} + \text{SiO}_{2(l)} \\
&\text{ii}_F: \text{Si}_{(l)} + \text{SiO}_{2(l)} \rightarrow 2 \text{SiO}_{(g)} \\
&\text{iii}: \text{SiC}_{(s)} + \text{SiO} \rightarrow \text{Si}_{(l)} + \text{CO}_{(g)}
\end{align*}

**Silicon: Si_{(l)}**

**Ambient Oxidizer**

\begin{align*}
&\text{CO}_{2(g)} \\
&\text{SiO}_{2(g)}
\end{align*}
Response Surface Methods

- RSM explores the relationships among input variables and one or more response variables.
- First proposed by Box and Wilson in 1951
- Uses designed experiments to map out a multi-dimensional surface which guides the user towards more optimal performance.
- Box and Wilson suggested that a quadric model to parameterize the response surface

1. Vary variables to explore search space
2. Map response
3. Move towards optimum

B. Erik Ydstie
Extremum Seeking Steady State Control

Model:

\[ J(t) = aJ(t-1) + g_0 + g_1 u(t-1) + g_2 u^2(t-1) \]

Adapt parameters using regression analysis

B. Erik Ydstie
The system is \[ J(t) = aJ(t-1) + g_0 + g_1 u(t-1) + g_2 u^2(t-1) \]

At steady state \[ J(t) = J(t-1) = J \]

Hence:

\[ J = \frac{g_0}{1-a} + \frac{g_1}{1-a} u + \frac{g_2}{1-a} u^2 \]

Solving \( \frac{dJ}{du} = 0 \) gives optimal input

\[ u^*(t) = -\frac{g_1}{2g_2} \]

B. Erik Ydstie
Y as a Function of U

Y

U

REAL

START

u(2)

u(6)

u(8)

B. Erik Ydstie
\[ y(t) = ay(t - 1) + g_0 + g_1 u(t - 1) + g_2 u^2(t - 1) \]

\[
\begin{align*}
  a &= 0.5 \\
  g_0 &= 0 \\
  g_1 &= 1.0 \\
  g_2 &= -0.2 \\
  J^* &= u^* = 2.5
\end{align*}
\]

B. Erik Ydstie
Step 1: Calculate adaptive model parameters using Least Squares
Step 2: Calculate $u_{\text{max}}$
Step 3a: Every N steps set $u(t) = u_{\text{max}}$
Step 3b: All other steps, excite the process by setting

$$u(t) = u(t - 1) + \Delta$$

where $\Delta$ is randomly selected between three points. $\Delta = \{-d, 0, d\}$
Plant Trials

\[ y(t) = a_1(t-1) + a_2 y(t-1) + b_1 u(t-d) + b_2 u(t-d-1) + c_1 u(t-d) + c_2 u(t-d-1)^2 \]

Use persistent excitation

Current average operating point

Silicon Production

Carbon Input
Poly-Crystalline Silicon Production

Silicon wafers

Solar Cells

Solar Modules

Metallurgical Silicon Production

Process flow diagram disproportionation and pyrolysis

$4 \text{SiHCl}_3 \rightarrow \text{SiH}_4 + 3 \text{SiCl}_4$

$\text{SiH}_3 + \text{Si} + 2 \text{H}_2$

High Purity Silane ($\text{SiH}_4$)

Solar Grade Silicon (SoG)

(About 385,000 tons, cost @ $20-30 per kg, 2012)

Hydrogen

$\text{SiHCl}_3$ or $\text{SiH}_4$
Poly-Silicon Production – a Roller Coast Ride

Metallurgical Grade $3-5 per kg

Electronic Grade $40-60 per kg

Raw Material

SiHCl₃ (TCS)

Distillation

Decomposition

Crystallization

Wafers

ICs

10% Waste

1998 Appx. 2000 tons per yr solar silicon $20 -25 per kg

Remelt/Cryst

Wafers

PV Cells

Modules and Installation

Poly-Silicon Production – a Roller Coast Ride

Metallurgical Grade $3-5 per kg

Electronic Grade $40-60 per kg

Raw Material

SiHCl₃ (TCS)

Distillation

Decomposition

Crystallization

Wafers

ICs

10% Waste

1998 Appx. 2000 tons per yr solar silicon $20 -25 per kg

Remelt/Cryst

Wafers

PV Cells

Modules and Installation
Raw Material: SiHCl$_3$ (TCS)  
Distillation

Decomposition

Crystallization

Wafers  ICs

Metallurgical Grade $3-5$ per kg

Electronic Grade $40-60$ per kg

Missing link

Insufficient too expensive

Remelt/Cryst

Wafers  PV Cells

Solar Grade Aim: $15$ per kg

2006 Spot Price $200 +$ per kg

2013 spot price $17.50$ per kg
Raw Material → SiHCl₃ (TCS) Decomposition → Crystallization → Distillation → Wafers

ELKEM ASA
Metallurgical Route

REC Silicon LLC
Chemical Route

New Products !!!!!

Solar Grade Aim: $15 per kg

ELKEM ASA
Purification by LLE/crystallization
Production Plant built 2009

Cost @ 15 per kg

Solar Grade Silicon LLC
Silane Decomposition in FBR
Production Plant built 2009

Cost @ $18 per kg

Metallurgical Grade $3-5 per kg → Electronic Grade $40-60 per kg
Solar Silicon Grade Silicon via the FBR process

From Silane to Solar Silicon

SiHCl$_3$ or SiH$_4$

SiH$_4(g)$ $\rightarrow$ Si$_{(s)}$ + 2H$_2(g)$

Si powder $\rightarrow$ H$_2$

SiH$_4$ H$_2$ Si

Siemens Reactor
Batch Process
1100°C (TCS)
650 °C (Silane)

Fluid Bed Reactor
Continuous Process
Large surface area
650 °C

Goal: develop scale-up and control models to optimize granular yield and control particle size.
The Population Balance

**Theorem 1:**
The discretized balances converge to the continuous population balance as the number of size intervals approaches to infinity.

Mass balance:
\[
\frac{dM_i}{dt} = f_{i-1} - f_i + r_i - \phi_i
\]

Number balance:
\[
\frac{dn_i}{dt} = \frac{f_{i-1}}{m_i} - \frac{f_i}{m_{i+1}} - \frac{\phi_i}{m_i}
\]
\[
f_i = \frac{m_{i+1}}{m_{i+1} - m_i} r_i
\]

\[
\frac{\partial n}{\partial t} + \frac{\partial (Gn)}{\partial l} = B - D + \frac{F_{in}}{V} n_{in} - \frac{F}{V} n
\]
Model Verification using Pilot Plant Data

Time constant for particle size distribution about 50 hours.

Weak control of distribution function

Difficult to control yield loss (sensitive system)
Scale-up models: from pilot to demonstration plant

Granular Product and Seed Mean Diameter Correlation

\[
\ln \left( \frac{D_{ap}}{D_{as}} \right) = \frac{1}{3} \left[ \ln \left( 1 + \frac{Y}{S} \right) - \ln \left( \frac{n_p}{n_s} \right) \right]
\]

Simulation Data Curve Fit:
\[
y = 0.332x + 0.002
\]
\[
R^2 = 1.000
\]

Y-Yield
S-silane feedrate
D- average diameter (p - product, s-feed)
n- particle feedrate (p - product, s-feed)
**Theorem 2:** The cumulative mass fraction at steady state is given by

\[ \Phi_m(l) = 1 - \exp\left(-\frac{l}{G'T}\right) \left(1 + \frac{l}{G'T} + \frac{1}{2} \left(\frac{l}{G'T}\right)^2 + \frac{1}{6} \left(\frac{l}{G'T}\right)^3\right) \];

the resulting particle mass distribution is defined as

\[ \phi_m(l) = \frac{d\Phi_m(l)}{dl} \text{ so that } \phi_m(l) = \frac{1}{6} \frac{l^3}{(G'T)^4} \exp\left(-\frac{l}{G'T}\right). \]

**Remark:** The cumulative number fraction at steady state is given by

\[ \Phi_n(l) = 1 - \exp\left(-\frac{l}{G'T}\right) \]

which corresponds to the residence time distribution for a continuous stirred tank reactor.
Cumulative mass fraction of silicon particle at steady state

\[ \Phi_m(l) = 1 - \exp \left( -\frac{l}{G_T} \right) \left( 1 + \frac{l}{G_T} + \frac{1}{2} \left( \frac{l}{G_T} \right)^2 + \frac{1}{6} \left( \frac{l}{G_T} \right)^3 \right); \]
Stability of Population Balance for Silicon Production

\[
\frac{\partial n}{\partial t} + \frac{\partial (Gn)}{\partial l} = B - D + \frac{F_{\text{in}}}{V} n_{\text{in}} - \frac{F}{V} n
\]

Stability analysis using Lyapunov function

\[
W = \frac{1}{2} \int_{0}^{\infty} \overline{m(l)^2} \, dl
\]

\[
\frac{dW(t)}{dt} = -\frac{c_s}{\rho V \Theta} \int_{l_{\text{min}}}^{l_{\text{max}}} \left( \frac{F}{V} - \frac{\rho}{lG} \right) \overline{m(l)^2} \, dl
\]

**Theorem 3:** Population balance converges to the stable steady state provided that the powder concentration is constant and

\[
\frac{V}{F} < \frac{G}{\rho} l_{\text{min}}
\]

- Small volume \( V \)
- High throughput \( F \)
- Large seed size \( l_{\text{min}} \)
- High growth rate \( G \)
Stability

- Developed method for scale-up and control
- Predict particle size distribution for product
- Stability conditions

Seed size larger than critical

Seed size smaller than critical

Figure 3: Radially distributed lines
• Christy starts thesis 2002
• Population and FBR modeling
• REC starts small pilot 2002
• Fluor involved in 2004
• Inventory control solves several control challenges
• Christy completes thesis 2007
• **REC Silicon $970 million expansion project** 24 fluid bed reactors to produce 6,500 metric tons of polysilicon per year

Current about <$20 per kg!!
Metallurgical Silicon Production → Poly-Crystalline Silicon Production → Silicon wafers → Solar Cells → Solar Modules

Czochralski Process

Sawing accounts for 30% of wafer fabrication costs and generates up to 50% of material losses.
Horozontal ribbon growth (HRG)

- Continuous process to produce 150 – 250 micron wafer
- Silicon floats on top of its melt
- No sawing, hence no material losses

**Challenges:**
- Crystallization and stability (micro-scale) to achieve single crystalline Silicon film
- Complex fluid flow and heat transfer interaction
- Impurity modeling
- Lack of experimental data and proof of concept
Horizontal ribbon growth

**Idea**
- William Shockley (1962)

**Experiments**
- Carl Bleil (GM, 1969)
- Bossi Kudo (Japan Silicon Co. Ltd, 1979)

**Theory**
- John Zoutendyk (JPL, 1978)

**Mathematical Modeling**
- Curtis Rhodes and collaborators (U. of South Carolina, 1980)
- Parthiv Daggolu, Andrew Yeckel, Carl Bleil and Jeff Derby (U. of Minnesota, 2012 & 2013)
Sensitivity study using multi-scale models

- Fluid flow and heat transfer model implemented using COMSOL (Eulerian)
- Crystallization dynamics implemented in MATLAB (Lagrangian)

AIM: Design a pilot scale plant for process verification

Scale-up models

Interaction between fluid flow and heat transfer

Crystallization dynamics

Interfacial Stability
Ice Machine validation

<table>
<thead>
<tr>
<th>Property</th>
<th>Silicon</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative density (liq/sol)</td>
<td>1.11</td>
<td>1.09</td>
</tr>
<tr>
<td>Relative heat capacity</td>
<td>0.93</td>
<td>2.05</td>
</tr>
<tr>
<td>Kinematic viscosity x10^-3</td>
<td>0.22</td>
<td>1.70</td>
</tr>
<tr>
<td>Relative thermal conductivity</td>
<td>3.23</td>
<td>0.26</td>
</tr>
<tr>
<td>Latent heat of fusion</td>
<td>0.70</td>
<td>0.33</td>
</tr>
</tbody>
</table>
Installation of HRG Pilot Plant at CMU

1. ~ $1M investment capital
2. ~$1.5M R&D (modeling small scale,..)
3. 60kW induction furnace
4. 5in wide
5. 10 ft long
6. Ar controlled atmosphere
7. Allen Bradely control system
Conclusions

• Price has come down to a level where solar technology competes successfully in some markets (with subsidies)
• Technology has been developed to reduce cost further
• New challenge: Increase efficiency (Si current ~18%)
• Reduce cost by 50%
• Multi-junction cells at 40% and higher
• Process systems engineering can play an important supportive role

• Solar power may be cheaper than electricity generated by fossil fuels and nuclear reactors within three to five years (2017) because of innovations,

  Mark M. Little, the global research director for General Electric Co. (GE)