<table>
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<th><strong>About HelioVolt</strong></th>
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<td><strong>Founded:</strong> 2001</td>
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<td><strong>Location:</strong> Austin, TX (HQ/R&amp;D Center &amp; 1\textsuperscript{st} Factory)</td>
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<td><strong>Employees:</strong> 100+</td>
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<td><strong>Technology:</strong> Rapid low-cost printing of high-efficiency CIGS photovoltaic integrated circuits (PVIC)</td>
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<td><strong>Funding:</strong> Raised $130M Private Equity Financing</td>
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- **Austin Prototype Development Facility (APDF) 38,460 ft\textsuperscript{2}**
- **Austin Factory 1 (AUSF1) 122,400 ft\textsuperscript{2}**
Cross Section of a Typical CIGS Solar Cell

Front Glass
Front Contact
Buffer (n-type)
Absorber (p-type)
Back Contact
Back Glass

Current collection grid

HR-ZnO/n^+-ZnO (0.5 μm)
CdS (0.05 μm)
Cu(InGa)Se_2 (2 μm)
Mo (0.5 μm)
Soda lime glass

ZnO:Al
i-ZnO
CdS
Cu(InGa)Se_2
Mo
Substrate


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Multisource Elemental Coevaporation of CIGS

Typical evaporation temperatures ranges:
- Cu: 1300 - 1400°C
- In: 1000 - 1100°C
- Ga: 1150 - 1250°C
- Se: 300 - 350°C

- Sequential process in which In & Ga are deposited separately from the Cu
- Approach A:
  - \((\text{InGa})_x\text{Se}_y\) deposited
  - Cu & Se deposited until film reaches desired composition
  - Layers interdiffuse to form \(\text{Cu(InGa)}\text{Se}_2\)
- Approach B (three-step coevaporation):
  - \((\text{InGa})_x\text{Se}_y\) deposited
  - Cu & Se deposited, Cu delivery continues until film has overall Cu-rich composition
  - In & Ga, in the presence of excess Se, are evaporated to achieve Cu deficiency
  - Layers interdiffuse to form \(\text{Cu(InGa)}\text{Se}_2\)

Produced highest efficiency cells (20%)
Improved performance attributed to:
- Band gap gradient resulting from Ga concentration decreasing from Mo back contact to surface
- Improved crystallinity of films

W.N. Shafarman et al., ‘\(\text{Cu(InGa)}\text{Se}_2\) Solar Cells’ in Handbook of Photovoltaic Science and Engineering (2003)
Metal precursor deposition is followed by selenization; many variations exist in both the precursor deposition and the Se reaction steps.

Metal precursor films are typically reacted in either H$_2$Se or Se vapor at 400 to 500°C for 30 to 60 minutes:

- Reaction in H$_2$Se has advantage of being feasible at atmospheric pressure and can be precisely controlled, but gas is highly toxic and requires special precautions.
- Reaction in a Se vapor can be obtained by thermal evaporation.
- Poor adhesion and formation of a MoSe$_2$ layer at the Mo/CIGS interface limit the reaction time and temperature.

Highest-efficiency selenization-produced cell reported (16.2%) used reaction in H$_2$Se, but there has been less effort at optimizing laboratory-scale cell efficiencies than with coevaporation.

Showa Shell and Shell Solar successfully scaled up this process to commercial production and demonstrated highest large-area CIGS module efficiencies (13.4%).
CIGS by Field-Assisted Simultaneous Synthesis and Transfer (FASST®) Process

Combines features of:
- Rapid Thermal Processing
- Anodic Wafer Bonding

Advantages:
- Rapid processing
- Low thermal budget
- Confinement of volatile Se
- High material utilization
- Electrostatic field effects on ionic constituent transport during synthesis
- Having two precursors allows independent optimization of:
  - Composition
  - Structure
  - Deposition method
  - Processing conditions

Two Stages
- Precursor deposition
- Rapid thermal processing & separation

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Recrystallization of Nanoscale Granular Precursor Films

Precursor Film

FASST® CIGS cross-section

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CIGS Phases

CuInSe$_2$ chalcopyrite crystal structure:
(a) conventional unit cell of height c, with a square base of width a
(b) cation-centered first coordination shell
(c) anion-centered first coordination shell showing bond lengths d$_{Cu-Se}$ and d$_{In-Se}$.

T–X section of the phase diagram along the Cu$_2$Se-In$_2$Se$_3$ pseudobinary section of the Cu–In–Se chemical system.

α: CuInSe$_2$ chalcopyrite phase
β: In-rich/Cu-poor (Cu$_2$In$_4$Se$_7$ & CuIn$_3$Se$_5$) ordered defect compound (ODC) phase
Observations on Device-Quality ($\eta > 15\%$) CIGS:

- Large columnar grains
- Copper deficiency compared to $\alpha$-CuInSe$_2$
- Compositions lie in the equilibrium $\alpha + \beta$ 2-phase domain: $\alpha$ domains, Cu-rich with $p$-type conductivity and $\beta$ domains, Cu-poor with $n$-type conductivity, form nanoscale $p$-$n$ junction networks*;
  - n-type networks act as preferential electron pathways,
  - p-type networks act as preferential hole pathways,
  - positive and negative charges travel to the contacts in physically separated paths, reducing recombination

*Intra-Absorber Junction (IAJ) model, APL 87, 121904 (2005)
Diffusion in CIGS Processing

- Diffusion in CIGS layer
  - Diffusion of Cu ions during CIGS formation
  - Equilibrium between Se atoms in CIGS, liquid Se & Se vapor
  - Relative diffusion of Ga & In
  - Interdiffusion of In-Ga-Se and Cu-Se layers
  - Diffusion creating composition gradient along CIGS film thickness
- Transport of Na from soda lime glass (SLG) through back contact into absorber layer
- Diffusion of Se into Mo back contact; some MoSe$_2$ helps contact resistance, too much affects adhesion & Mo-CIGS electrical contact
- Diffusion of buffer elements (e.g., Cd, Zn, In) into absorber
Diffusion in CIGS Processing

Modeling diffusion phenomena in CIGS and developing a fundamental understanding of the effect of process parameters on composition gradients and band gap gradings, and their effect on device performance, is key to achieving controllable steady improvement in conversion efficiencies, and repeatable uniform high-yield high-performance PV modules manufactured in large volume at high speed and low cost.
Thank you!

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