Diffusion in Cu(In,Ga)Se$_2$
Photovoltaic Absorber Formation

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Outline

■ Cu(In,Ga)Se₂ photovoltaics overview
■ Diffusion reaction study using in-situ HT-XRD
  → CuSe/GaSe → CuGaSe₂
  → Cu-In + Se → CuInSe₂
■ Preliminary study of DICTRA diffusion modeling
  → Cu-In + Se → CuInSe₂
■ Summary
Thin Film CIGS Solar Cells

Building-integrated CIGS, 85kW Shell Solar

Flexible, lightweight Cu(InGa)Se₂ - Global Solar
Best Efficiency of Thin Film Cells

- Cu(In,Ga)Se₂
- CdTe
- a-Si

- Boeing
- AMETEK
- Photon Energy
- Univ. of So. FL
- Kodak
- Monosolar
- Matsushita
- BP Solar
- EuroCIS
- NREL
- Univ. of Maine
- Boeing
- ARCO
- AMETEK
- United Solar
- ECD
- RCA
- Univ. of So. FL
**Cu(In,Ga)Se₂ Solar Cells**

- Most promising thin film photovoltaic material

  - $\eta = 19.9\%$, NREL (2008)
  - Direct band gap
    - band gap engineering ($E_g \sim 1.2$ eV at $x(Ga)=0.3$)
  - High optical absorption coefficient
    - thin film $\sim 2\ \mu m$
  - High radiation resistance
  - High reliability

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**Cu(In,Ga)Se₂ Solar Cells**

- **Chalcopyrite CIGS structure**
  - Substrate (Soda lime glass)
  - TCO (200~500 nm)
  - n-CdS (50 nm)
  - p-CIGS absorber (2 $\mu m$)
  - Mo (~0.5 $\mu m$)
  - AR coating
  - Ni/Al grid

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**Typical device structure**
**Cu-In-Se Phase Equilibrium**

**Wide composition tolerance of chalcopyrite $\alpha$-CuInSe$_2$**

$x$(Cu) = 21~25 at.%

$\delta$: CuInSe$_2$ – sphalerite

$\beta$: CuIn$_3$Se$_5$ – ODC

$\gamma$: CuIn$_5$Se$_8$ – ODC

*T. Gödecke et al., Z. Metallkd (2000)*
Common Deposition Techniques

- Co-evaporation of elements (PVD, MBE etc.)
  : Cu, In, Ga, Se
  → *Highest efficiency!!*

- Rapid thermal process (RTP) of stacked or elemental precursors

- Selenization of metallic precursors: *"Shell Solar" 2 step method*

[Diagram of deposition processes and materials]
Diffusion Issues

- Selenization of metallic precursors: "Shell Solar" 2 step method

Ga accumulation at back!

Decrease device performance!
**Diffusion Issues**

\[ \text{Cu-Ga-In/Mo} \xrightarrow{\text{H}_2\text{Se} / \text{H}_2\text{S}} \text{Cu(In,Ga)(Se,S)}_2/\text{Mo} \]

**Complete \( \text{H}_2\text{Se} \) reaction prior to \( \text{H}_2\text{S} \)**
- Ga segregated to back

**Partial \( \text{H}_2\text{Se} \) reaction prior to \( \text{H}_2\text{S} \)**
- Ga distributed through film

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*G. Hanket, W. Shafarman, R. Birkmire. , Proc. 4th World Conf. on PVEC (2006).*
Reaction pathways and kinetics using *in-situ* HT-XRD
Precursor Diffusion Couples

- **Cu+Se**
  - Glass
  - $x_{Se} \approx 0.71$

- **In+Se**
  - Glass
  - $x_{Se} \approx 0.80$

- **Ga+Se**
  - Glass
  - $x_{Se} \approx 0.86$

- **Se**
  - **Cu**
  - Glass
  - $x_{Se} \approx 0.67$

- **Se**
  - **In**
  - Glass
  - $x_{Se} \approx 0.81$

- **Se**
  - **Ga**
  - Glass
  - $x_{Se} \approx 0.80$
Precursor Diffusion Couples

- \( \text{CuSe} \) on \( \text{In}_2\text{Se}_3 \) in Glass
- \( \text{CuSe} \) on \( \text{InSe} \) in Glass
- \( \text{Cu+Se} \) on \( \text{InSe} \) in Glass

- \( \text{Cu+In+Se} \) in Glass

- \( \text{Cu+In} \) in Glass

- \( \text{Cu+Ga+Se} \) in Glass

- \( \text{Cu+Ga} \) in Glass

- \( \text{CuSe} \) on \( \text{GaSe} \) in Glass
CuGaSe$_2$ formation from a bilayer GaSe/CuSe diffusion couple
Precursor Preparation by MEE System

- Ultra high vacuum system
- Operating pressure: ~ $10^{-8}$ Torr

- Rotating platen with 9 substrates:
  - $2'' \times 2''$ square, $2''$ circular
- Sequential deposition:
  - Heating $\rightarrow$ Cu $\rightarrow$ In $\rightarrow$ Ga $\rightarrow$ (Na) $\rightarrow$ Se
HT-XRD System

A: Spot-welded thermocouple
B: Heater strip (Pt20%Rh)
C: Sample

High Temperature Materials Laboratory of Oak Ridge National Lab.
Precursor Structure

![Graph showing CuSe: JCPDS #34-0171 with peaks at CuSe (006), CuSe (102), CuSe (101), CuSe (110), CuSe (108), CuSe (116), and a TEM image showing layers of CuSe, GaSe, and Glass.](image-url)
Temperature ramp anneal

CuSe + GaSe $\rightarrow$ Cu$_{2-x}$Se + Se + GaSe (or Ga$_2$Se$_3$) $\rightarrow$ CuGaSe$_2$

amorphous
**Isothermal annealing**

**Assumption:**

- Maximum peak area = 100 % reaction
- Normalized peak area = fractional reaction
Solid-state Growth Models

• Parabolic growth model

Before reaction

Nucleation at A-B interface

Diffusion thru product & reaction (ex. $D_{BC} > D_{AC}$)

$$\frac{dy}{dt} = \frac{D \cdot k}{y}$$

$y^2 = k_p \cdot t$

• Avrami growth model

Phase A Covered with B

Nucleation

Diffusion & growth

$x = 1 - \exp[-(kt)^n]$

$\ln[-\ln(1-x)] = n \ln t + n \ln k$

$0.5 < n < 1.5$

(1-D diffusion)
Modified Avrami Analysis

\[ \alpha = 1 - \exp[-(k(t+t^*))^n] \]
Kinetic Analysis

Parabolic model

Modified Avrami model

\[\alpha^2 \sim k \cdot t\]

\[\ln[-\ln(1-\alpha)] = n \ln(t+t^*) + n \ln k\]

Analysis suggests one-dimensional diffusion controlled reaction
TEM-EDS

Isothermal annealing

- **T = 280 °C**
- **T = 300 °C** *(t~30 min)*
- **T = 340 °C**
- **T = 370 °C**

**TEM-EDS**
TEM-EDS Analysis

Glass/GaSe/CuSe Precursor

EDS line scan

Pt
CuSe
GaSe
Glass

Se
Cu
Ga

distance (µm)
TEM-EDS Analysis

Glass/GaSe/CGS/CuSe annealed for 30 min, at 300 °C

EDS line scan

Ga gradient !!

Ga  Cu  Se

0  0.2  0.4  0.6
distance (μm)

A  B
CuInSe$_2$ formation from selenization of Cu-In precursor

Cu-In
Glass

Se vapor

Reactive annealing

CIS
Glass
HT-XRD with Selenization Chamber

Panalytical Philips X’pert system

Sample holder

Selenium powder
Precursor sample
Aluminum foil
Nickel wire

Capton/Be window
Surrounding Heater
Sample holder

X-ray tube
PSD
Chamber

CW in out

In Out (He)

High Temperature Materials Laboratory, ORNL
Selenization Chamber

Aluminum foil

- Selenium powder
- Precursor sample
- Aluminum foil
- Nickel wire

◆ Al foil:
- (1) Loss of X-ray intensity
- (2) Possible reaction with Se above 650°C

◆ Graphite dome:
- (1) Easy to handle
- (2) Extremely X-ray transparent
- (3) High stability
**SEM / EPMA**

### Precursor

- [Cu] / [In] ~ 1.0
  - Cu-In
  - Mo
  - Glass

### Selenized CIS

- CuInSe₂
  - MoSe₂
  - Mo
  - Glass

#### Island (In-rich)

#### Matrix (Cu₂In + CuIn)

#### EPMA Results (Va=6 keV)

<table>
<thead>
<tr>
<th></th>
<th>Matrix</th>
<th>Island</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (at.%)</td>
<td>59.4 (±1.2)</td>
<td>36.0 (±1.0)</td>
</tr>
<tr>
<td>In (at.%)</td>
<td>40.6 (±1.2)</td>
<td>64.0 (±1.0)</td>
</tr>
</tbody>
</table>

- Island: In-rich or nearly pure indium phase
XRD & GI-XRD for Precursor

\[ \theta - 2\theta \]

\[ \omega = 1^\circ \]
\[ \omega = 0.5^\circ \]

Cu\textsubscript{2}In (101)
Cu\textsubscript{2}In (102)
Cu\textsubscript{2}In (-134)

Mo (110)

Indium
(Cu+In)/Mo Selenization

CuInSe₂ (112)
MoSe₂ (004),(100)
Mo (110)
CuInSe₂ (312)
MoSe₂ (312)
MoSe₂ (105)
MoSe₂ (110)

CuSe→CuSe₂

500 °C
440 °C
300 °C
230 °C
90 °C
25 °C

[Cu]/[In]~1

Mo → MoSe₂
CuSe₂ → CuInSe₂
Cu→CuSe→CuSe₂

(Cu + In)/Mo
\[(\text{Cu+In})/\text{Mo Selenization}\]

\[
\text{Cu/In} \rightarrow \text{CuSe} \rightarrow \text{CuSe}_2 \rightarrow \text{CuInSe}_2
\]
Isothermal Selenization

Temperature = 280 °C

Assumption for kinetic analysis

- Largest peak area = 100% reaction
- Fractional reaction = normalized peak area
Kinetic Analysis

\[ \ln[-\ln(1-\alpha)] = n \ln(t) + n \ln k \]

Analysis suggests one-dimensional diffusion controlled reaction
DICTRA Modeling

Concentration profile

Diffusion models

Solve the multi-component diffusion equations

Diffusion coefficients

\[ D = M \cdot \frac{\partial \mu}{\partial c} \]

Database

Mobility

DICTRA

Gibbs energy

Thermo-Calc
**Assumption:**

- Driving force: Gradient of Se chemical potential
- Control step: Diffusion of Se thru CIS layer
- Simplified pseudo-binary reaction: $\text{Culn} + 2\text{Se} \rightarrow \text{CulnSe}_2$

Instead of: $m\text{Cu}_2\text{In} + n\text{CuIn} + m\text{In} + (4m+2n)\text{Se} \rightarrow (2m+n)\text{CuInSe}_2$
Cu-In Thermodynamic Database

H. S. Liu, et al., J. Phase Equilib. 23 (2002) 409
**DICTRA Optimization Results**

**Mobility parameter in DICTRA**

\[ MQ = -Q_B + RT\ln(M_B^0) \]

- \( Q_B \): activation enthalpy  
  \( (= 136,725 \text{ J/mol}) \)

- \( M_B^0 \): frequency factor  
  \( (= 0.01406) \)
Summary

- *In-situ* HT-XRD was successfully employed to investigate the reaction pathways and kinetics of binary and ternary diffusion couples.

- Kinetic data was used to get Se mobility database using DICTRA optimization.

- Systematic efforts on Cu-In-Ga-Se diffusion database establishment will be necessary to optimize high quality CIGS formation process.
Appendix
Region | Equilibrium phases
--- | ---
1 | $\alpha$-ClSe$_2$ + $\alpha$-Cu + $\beta$-Cu$_2$Se
2 | $\alpha$-ClSe$_2$ + $\alpha$-Cu + Cu$_7$In$_3$
3 | $\alpha$-ClSe$_2$ + Cu$_2$In + Cu$_7$In$_3$
4 | $\alpha$-ClSe$_2$ + Cu$_2$In + In$_4$Se$_3$
5 | $\alpha$-ClSe$_2$ + InSe + In$_4$Se$_3$
6 | $\alpha$-ClSe$_2$ + InSe + $\delta$-CuInSe$_2$
7 | $\alpha$-ClSe$_2$ + $\beta$-CuIn$_3$Se$_5$ + $\delta$-CuInSe$_2$
8 | $\alpha$-ClSe$_2$ + $\beta$-CuIn$_3$Se$_5$ + Liquid
9 | $\alpha$-ClSe$_2$ + $\beta$-Cu$_2$Se + Liquid

**Wide composition tolerance!!**

$x(Cu) = 21$-$25$ at.%

**Isothermal section at 500 °C**
Best Efficiency of Solar Cells

- **Multijunction Concentrators**
  - ▼ Three-junction (2-terminal, monolithic)
  - ▲ Two-junction (2-terminal, monolithic)

- **Crystalline Si Cells**
  - ■ Single crystal
  - □ Multicrystalline
  - ◼ Thin Si

- **Thin Film Technologies**
  - • Cu(In,Ga)Se₂
  - ○ CdTe
  - ○ Amorphous Si:H (stabilized)

- **Emerging PV**
  - ◤ Organic cells

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NIST Diffusion Workshop
May 12, 2008
Ga addition?

**Lattice constants**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice constant (a), nm</th>
<th>Lattice constant (c), nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuInSe$_2$</td>
<td>0.5784</td>
<td>1.1614</td>
</tr>
<tr>
<td>CuGaSe$_2$</td>
<td>0.5596</td>
<td>1.1002</td>
</tr>
</tbody>
</table>

**Bandgap energy**

$E_g(x) = 1.018 + 0.575x + 0.108x^2$

**Absorption coefficient**

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\alpha$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuInSe$_2$</td>
<td>$\sim 1 \times 10^5$</td>
</tr>
<tr>
<td>CuGaSe$_2$</td>
<td>$&gt;3 \times 10^4$</td>
</tr>
</tbody>
</table>
Binary Phase Diagram

Cu-Se

Ga-Se

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Diffusivity and Mobility

Diffusion coefficients are obtained as a product of a thermodynamic ($\frac{\partial \mu}{\partial c}$) and a kinetic ($M$) factor.

\[ D = M \cdot \frac{\partial \mu}{\partial c} \]

\[ M = M_b + \exp \left( \frac{M_q}{RT} \right) \]
Formation of CIS by selenization of Cu+In precursor

- Driving force: Gradient of chemical potential of Se
- Control step: Diffusion of Se thru CIS layer
- Key data:
  - Chemical potential of Se in different phases
  - Mobility of Se in CIS phase

- DICTRA optimization results:
  $M_b = 0$
  $M_q = -168000 \text{ J/mol}$

$M_q$ remains constant for the entire range of experimental temperatures.