Development of $CuInGaSe_2$ Thin Films for Solar Cell Applications

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US PVMC Program

US Department of Energy PV Manufacturing (PVMC) Initiative – A Path Towards Supply Chain Collaboration in the US

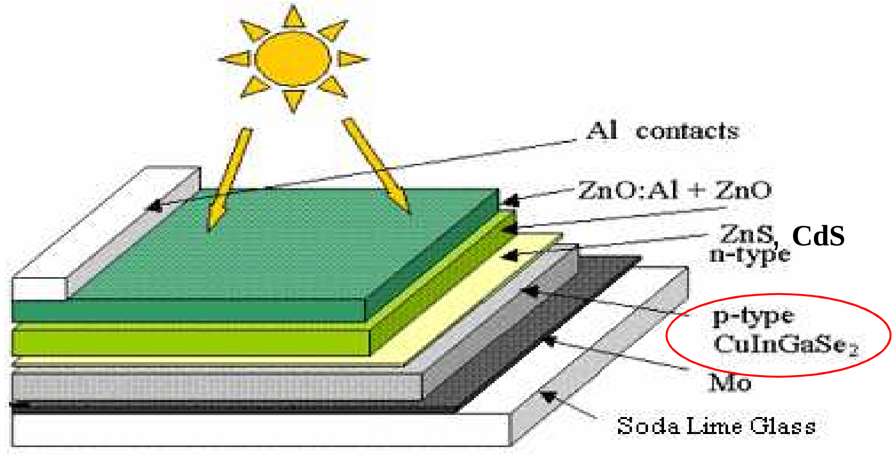
- Hybrid of industry-led consortium and manufacturing development facility (MDF) models in New York State with capabilities for collaborative and proprietary activities
- Overall investment of $300 M over 5 years from DOE, Industry, NY State.
- Focus on leading solar PV technology – CuInGaSe (CIGS) thin films – and manufacturing methods

- Expertise of primary partners – SEMATECH, CNSE – in consortium management, technology development, manufacturing productivity, and workforce development
- Breadth of support – partnership with ~80 companies and organizations throughout CIGS industry supply chain

Typical $Cu(InGa)Se_2$ Device Structure

- **Substrate**:
  - Soda lime glass – Na source, good thermal expansion match to CIGS, low cost
  - metal foil such as 300 or 400 series stainless steel – flexible, conductive
- **Back contact layer:** Mo, DC sputtered (0.5-1µm)
- **p-type absorber layer:** CIGS, CIAS direct band gap 1 - 1.26eV, DC co-sputtering followed by selenization with Se/Ar vapor/gas mixture (1-2µm)
- **n-type buffer layer:** CdS or ZnS, chemical bath deposition (50nm)
- **Window layer:** ZnO (50nm) and ZnO:Al (200nm), two layers one with high doping and other with low doping, , RF sputtered
- **Top contact/Grid:** Ni/Al, e-beam evaporation (1µm)

CIGS offers lower manufacturing cost while efficiencies are comparable to multi-crystalline Si based devices



Cross section of thin-film CIGS based solar cell device

The Cu/(In+Ga) ratio is favorite to be 0.88-0.95 in the precursor (NREL)

The Ga/(Ga+In) ratio is favorite to be 0.25-0.30 in the precursor (NREL)

Emphasis is given on the deposition of the p-type CIGS, CIAS absorber layer

www.energy.gatech.edu/presentations/tsurek.pdf

Thin Film Solar Cells (TFSC)

- **Low cost materials**
  - Film thickness 1 – 10μm (c-Si cells thickness 200-300 μm)
- **High through put manufacturing**
  - Monolithic integration for modules allows glass in/module-out production
  - Can use flexible substrate with roll-to-roll processing
- **Direct bandgap materials with high absorption coefficient**
  - Compositional tolerance: Cu at. % can vary from 22 to 25 at. %
  - Alloy with Ga, Al, S to engineer band gap 1.04 < Eg < 1.68 eV for 0< = Ga/(In+Ga)< =1

Typical I-III-VI_2 materials

	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	Efficiency (%)	Comments
CuInSe*	0.491	40.56	75.15	**15.0**	NREL
CuInGaSe*	0.694	35.1	79.52	**19.9**	NREL
CuGaSe*	0.823	18.61	66.77	**10.2**	NREL
CuInAlSe*	0.621	36.0	75.50	**16.9**	IEC
CuInGaS**	0.830	20.9	69.13	**12.0**	FSEC (Dhere)
CdTe	0.845	26.1	75.5	**16.7**	NREL

Current state of the art in device level

*Multi-stage co-evaporation, **Sulfurization of precursors
FSEC- Florida Solar Energy Center, IEC- Institute of Energy Conversion, NREL – National Renewable Energy Laboratory

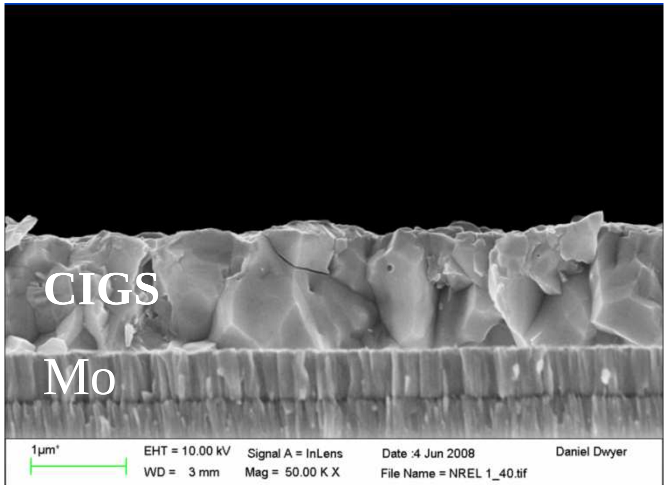
- The challenge is whether TFSC can demonstrate on large areas their potential for low cost at sufficient performance to compete in select markets with Si

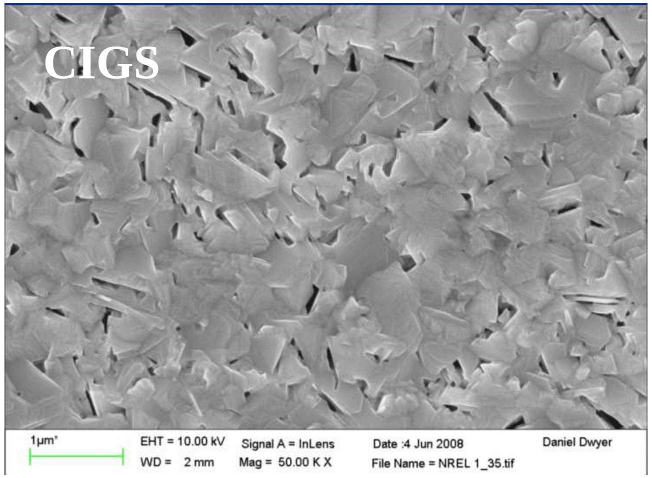
Rommel Noufi and Ken Zweibel, CdTe and CIGS Thin Film Solar Cells: Highlights and Challenges, NREL Report, (2007)
J. AbuShama, R, Noufi, and S Johnson, PVSC (2005)
M. A. Green et al., Prog. Photovolt. 17 85 (2009)

V_{oc}: open circuit voltage
J_{sc} : short circuit current density
FF : Fill factor

Research Goals

- Develop of a relative simple, reproducible, and easy to scale up 1-stage and 2-stage deposition techniques to enable the fabrication of CIGS and CIAS thin-film solar cells
  - Design the proper combination of substrate, barrier, and seed layers as a template for CIGS growth
    - Define the best processes for deposition of those layers
    - Transfer those processes to reel-to-reel equipment
  - Develop a process to co-sputter CuInGa and CuInAl precursor films of target composition
    - Selenize precursor film using elemental selenium or H_2Se to produce CIGS and CIAS films
- Correlate process parameters and film characteristics to PV device performance

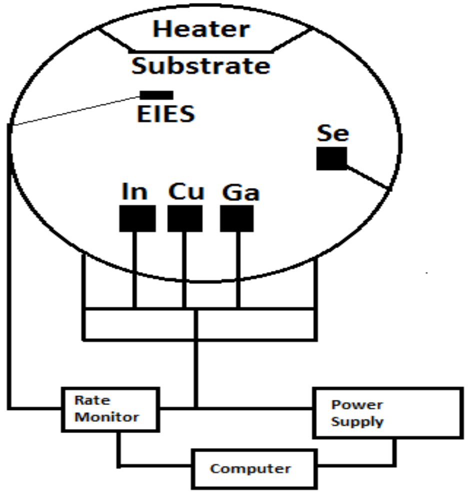




Cross-section and top view SEM images of CIGS films on Mo/glass

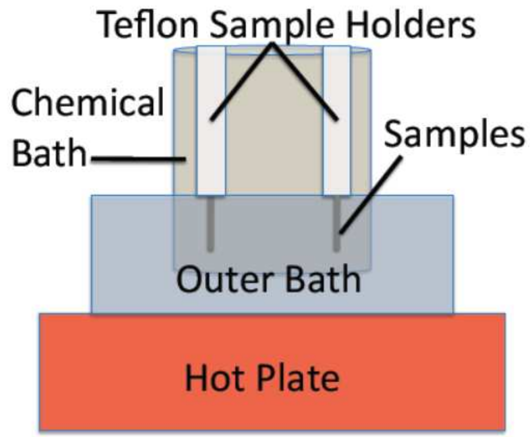
CIGS Evaporation and CdS - Experimental setup

1-step CIGS Deposition Process



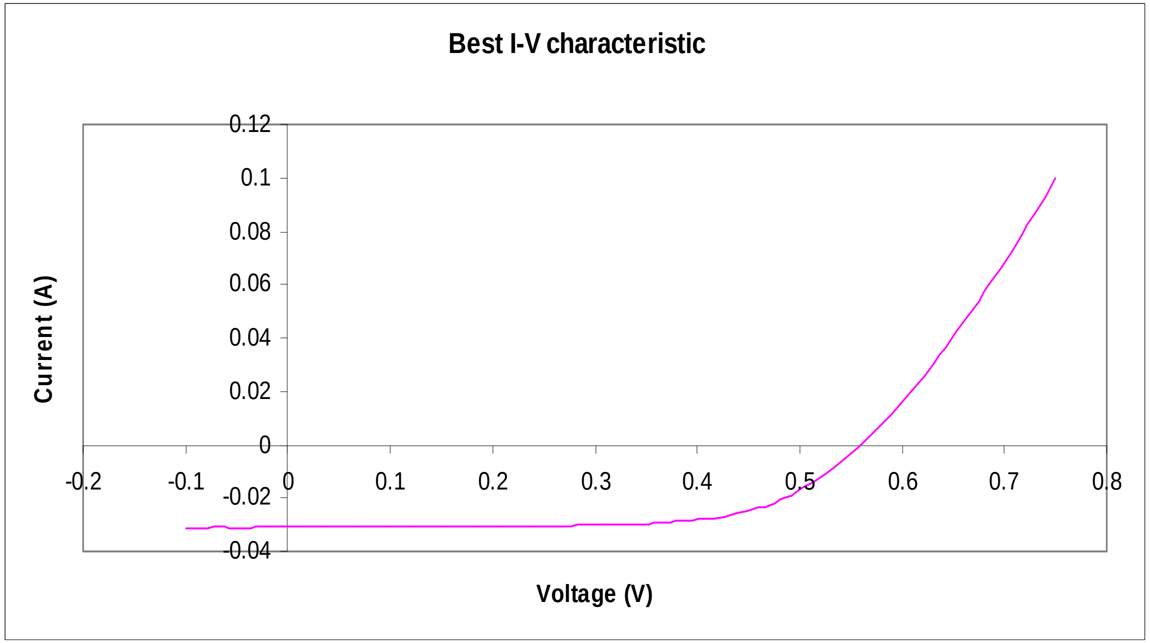
- Develop thermal evaporation that produces high efficiency thin film solar cells and has the lowest materials costs with high material utilization driving down the manufacturing cost per watt.
- Thermal evaporation of elemental Cu, In, Ga, and Se.

Chemical Bath Deposition (CBD) of CdS



- Evaluate the simultaneous development of new buffer layers using CBD methods to increase cost-efficiently using more acceptable and cheaper raw materials than CdS
- CdS Bath, 65^{o}C, DI Water, Ammonium hydroxide, Cd sulfate, thiorea
- Develop InS and ZnS as replacement of CdS

I-V Characteristics of Evaporated CIGS



V_{oc} – 558 mV
I_{sc} – 31.0 mA
FF – 66.19%
Eff – 10.40%

- I-V curve of CIGS Device

Sample ID	Efficiency Grid # (%)									Avg %
CIGS-s8-2	7.62	9.83	9.01	10.28	10.23	10.40	10.21	10.07	9.99	
	10.05	9.98	9.95	9.95	9.98	9.80	9.50	8.92	8.26	9.67

V_{oc} – Open circuit voltage
I_{sc} – Closed circuit current
FF – Fill Factor
Eff - Efficiency

Sputtering Thin Film CIGS: Deposition Goals

- Sputtering followed by batch selenization process (2-step process)
  - High-throughput of 4 x 6 ft. monolithic modules
  - Higher module compositional uniformity

- Develop a process to sputter high quality CuInGa precursor thin films
  - Target Composition: **Cu at. % : 48.7 - 46.8**
    In at. % : 37.2 - 35.9
    Ga at. % : 16.0 – 15.4

$$0.88 < \frac{Cu}{(In+Ga)} < 0.95 \quad 0.25 < \frac{Ga}{(In+Ga)} < 0.30$$

Monolithic Modules

  - Homogeneous and dense films with smooth surface morphology

Repins, et. al., Characterization of 19.9%-Efficient CIGS Absorbers, NREL report (2008)
M. E. Beck et al., Solar Energy Materials and Solar Cells, (2000)

CuInGa Precursor Co-sputtering

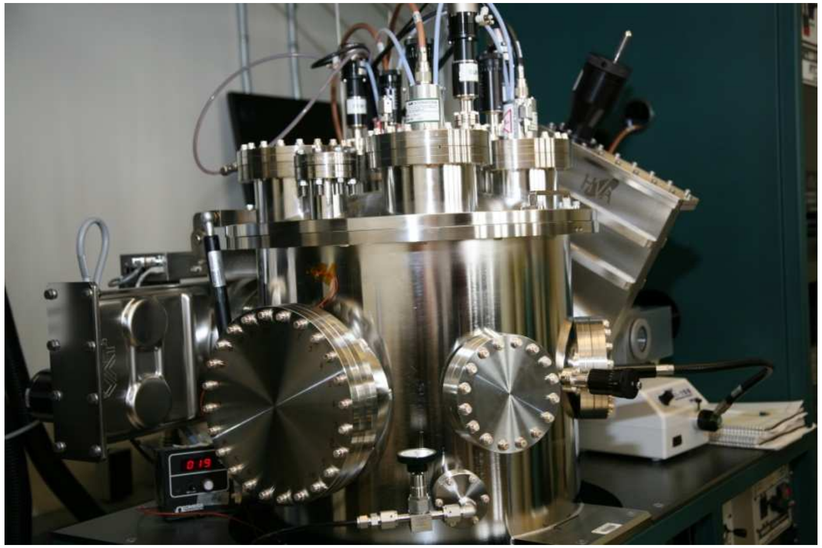
CuInGa Precursor – Co-Sputtering

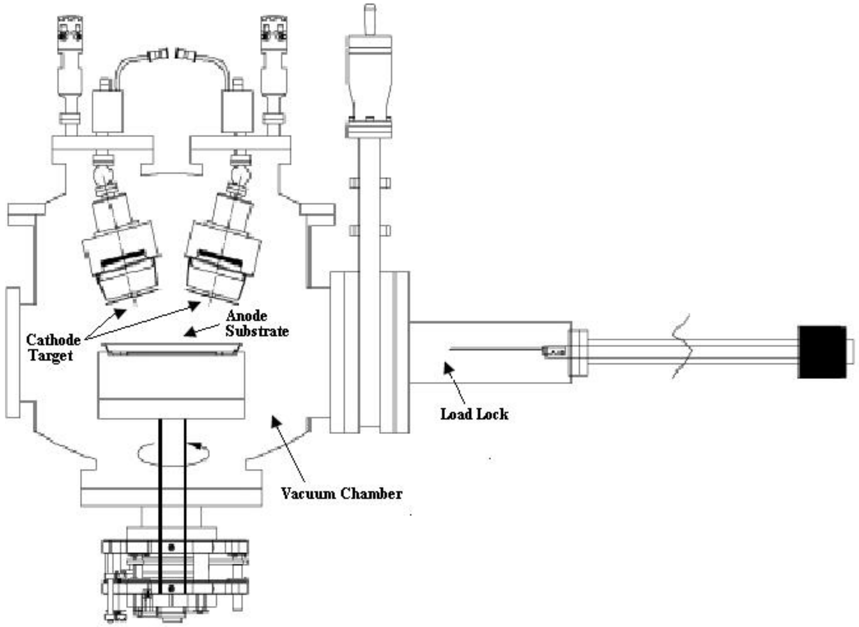
Con-focal sputtering guns allow simultaneous deposition of precursors resulting in more uniform film composition

RF/DC sputtering tool with:

<u>Two target approach</u>:

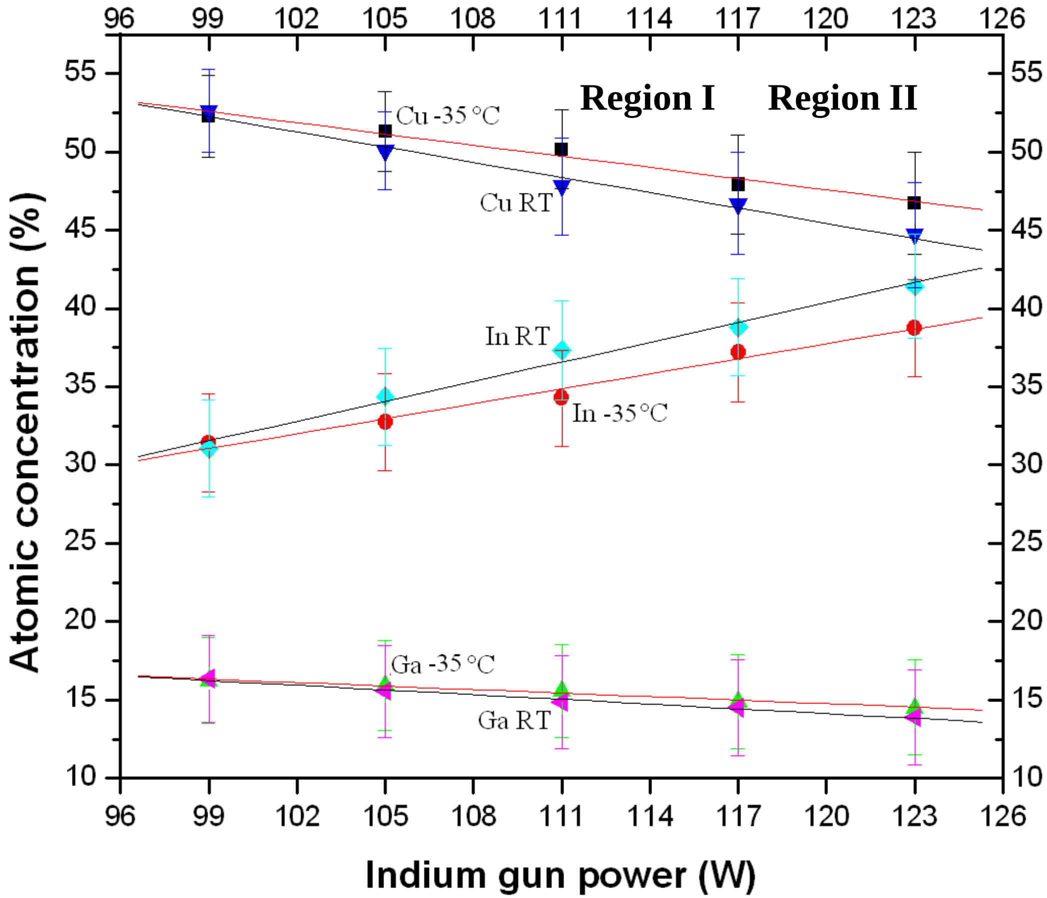
- **CuGa target (75/25 at. %)**
- **In target**





Process Parameter Investigation

Performed In target sputtering power study to identify the process conditions leading to desired CIG film composition and surface morphology



Process Parameters	Range
Power CuGa target In target	 138 Watt 99 – 123 Watt
Substrate Temp.	RT, -35°C

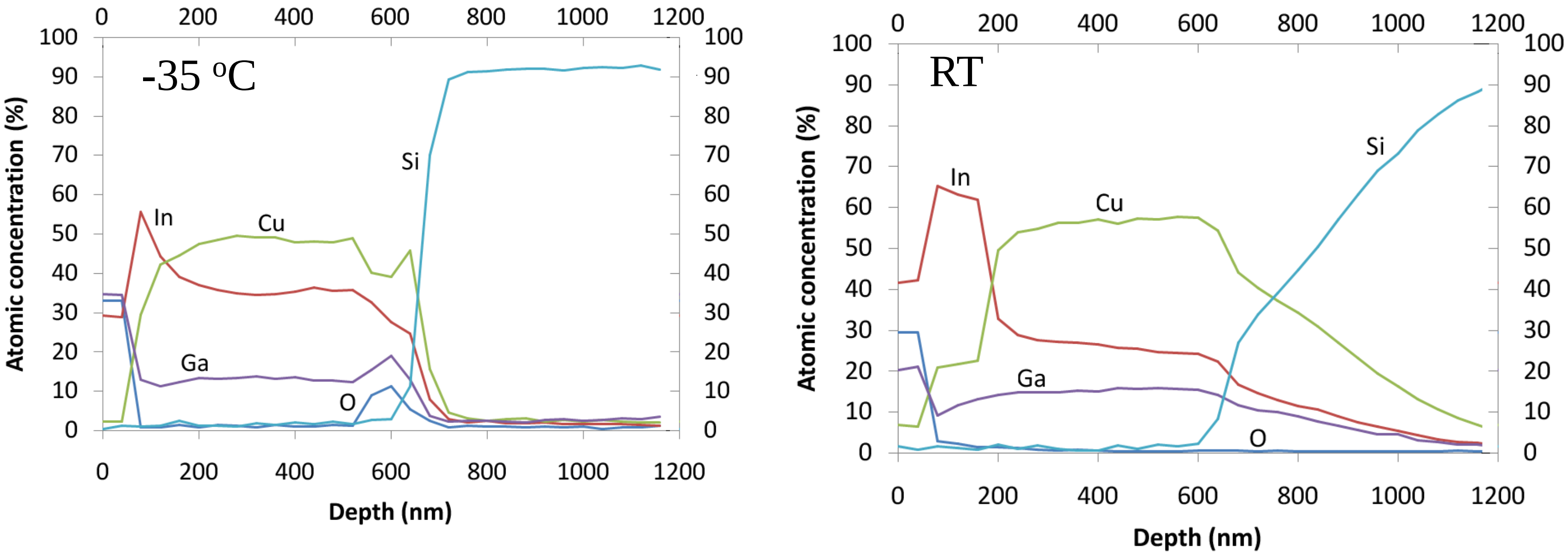
RT Deposition: Power range 111 – 117 W

Low Temp. Deposition, Power range: 117 – 123 W

Ref.: M. Hansen, H. Efstathiadis, P. Haldar, Thin Solid Films (2009)

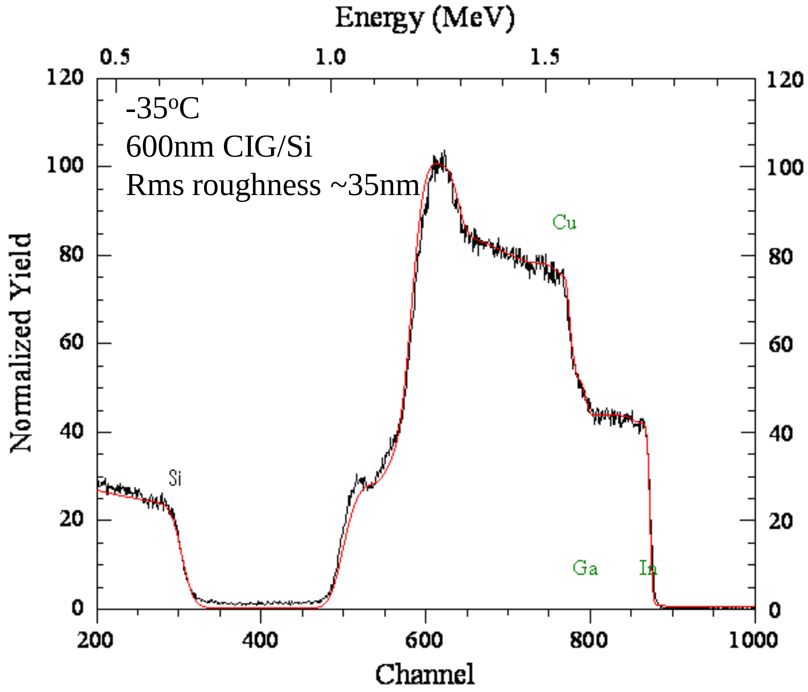
Composition of CIG Films

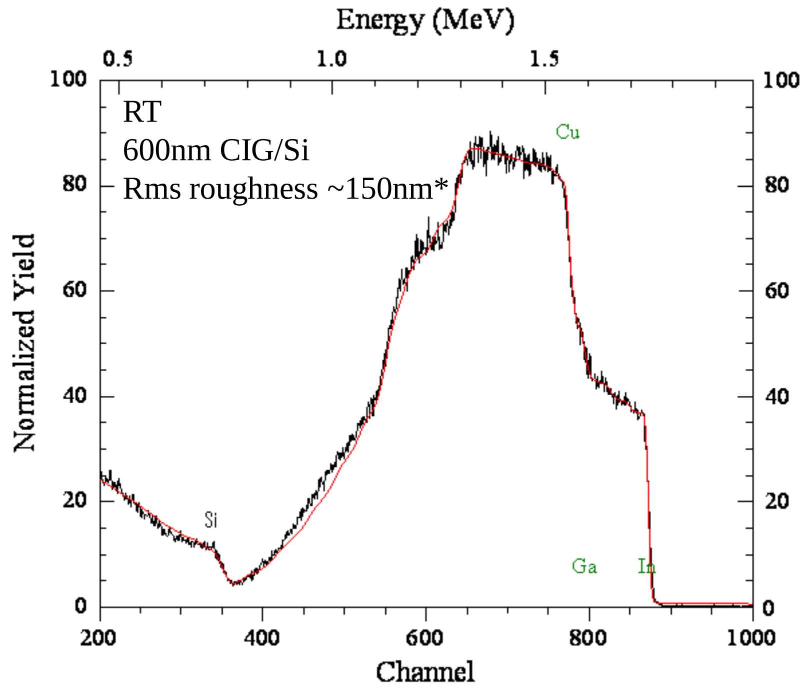
Auger Electron Spectroscopy composition depth profile of CuInGa precursor films on Si substrate



- At low substrate temperature, In segregates toward the surface at a lower rate compared to precursor films deposited at room temperature on Si substrate
- At RT deposition, In atomic concentration increases from 22 to 32 at. % while the Cu:Ga ratio is roughly 3:1

RBS Spectra of CIG Films





Atom	Average atomic %
Cu	0.49
In	0.36
Ga	0.15

$$\frac{Cu}{(In+Ga)} = 0.95$$ Target value: 0.88 - 0.95

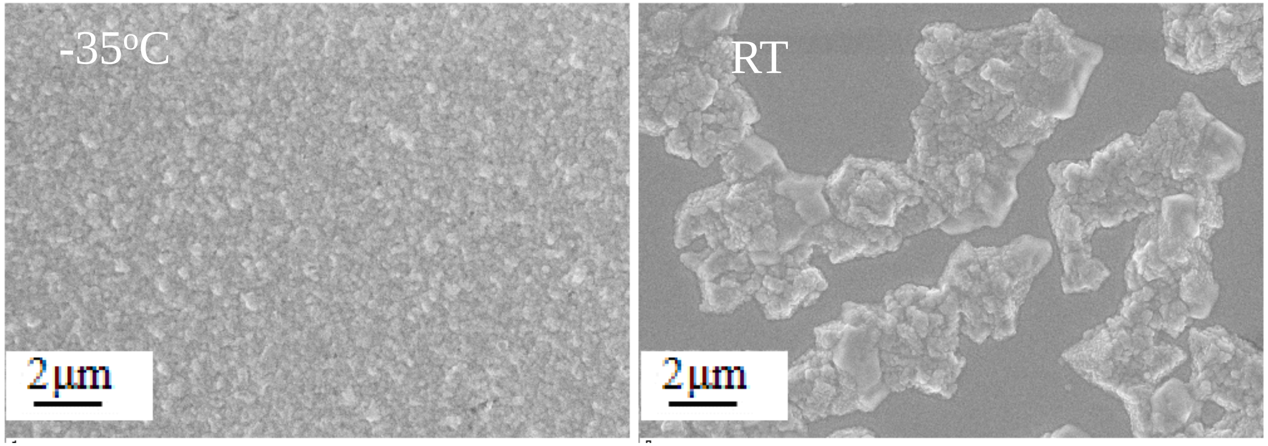
$$\frac{Ga}{(In+Ga)} = 0.29$$ Target value: 0.25 - 0.30

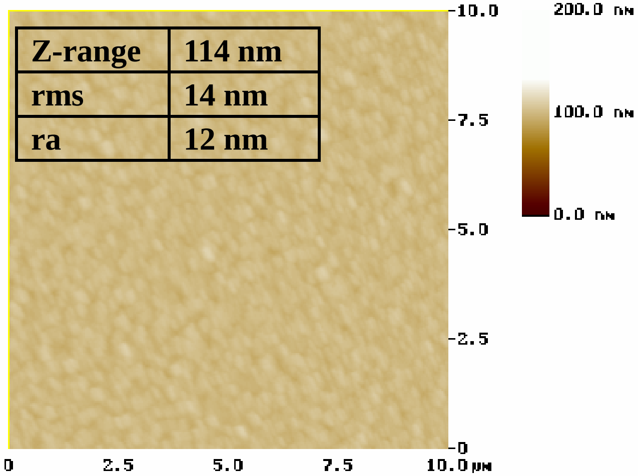
- **The flat In step from channels 800 to 870 shows an absence of an In concentration gradient versus depth**
- **The sharp drop off of the Cu, In and Ga steps in the channel range of 450 to 550 indicates a smooth surface morphology**
- **The sharp increase of In at the Si interface from channels 600 to 650 is due to the In rich phases sticking out of the surface**

*Obtained by AFM,
RBS: Rutherford Back Scattering

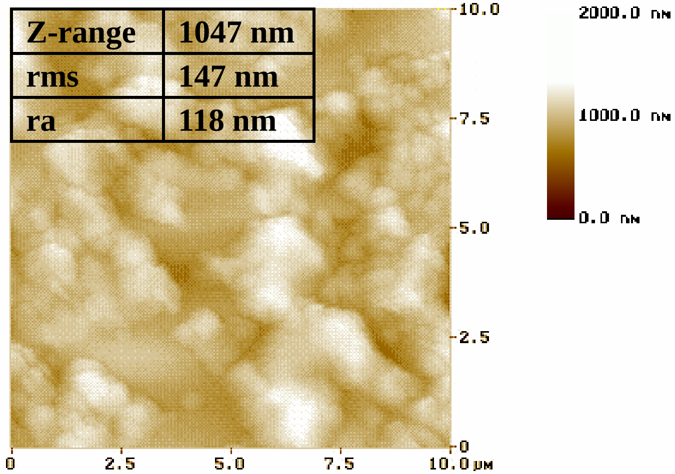
CIG Films - Surface Morphology

SEM images of precursor thin films with the desired chemical composition deposited at different temperatures





Z-range	114 nm
rms	14 nm
ra	12 nm

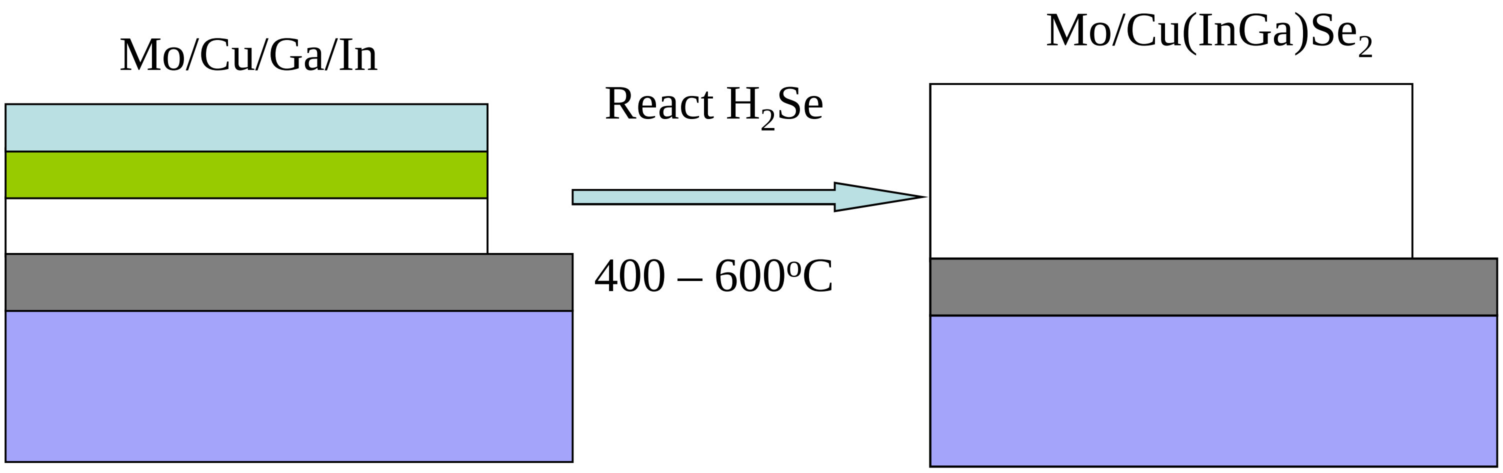


Z-range	1047 nm
rms	147 nm
ra	118 nm

Depositing at -35°C instead of RT reduces the rms surface roughness values by approximatelly an order of magnitude.

CIGS Deposition – Precursor Reaction

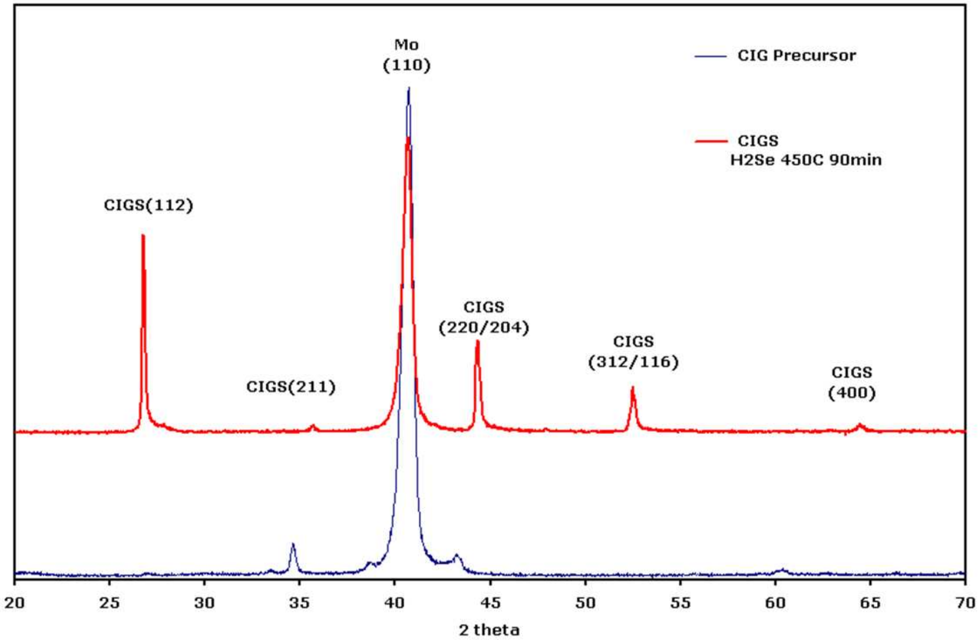
- Precursor with Cu, In, Ga - many deposition options
  - Criteria: low cost, uniformity, materials utilization
    - sputtering - commercially available

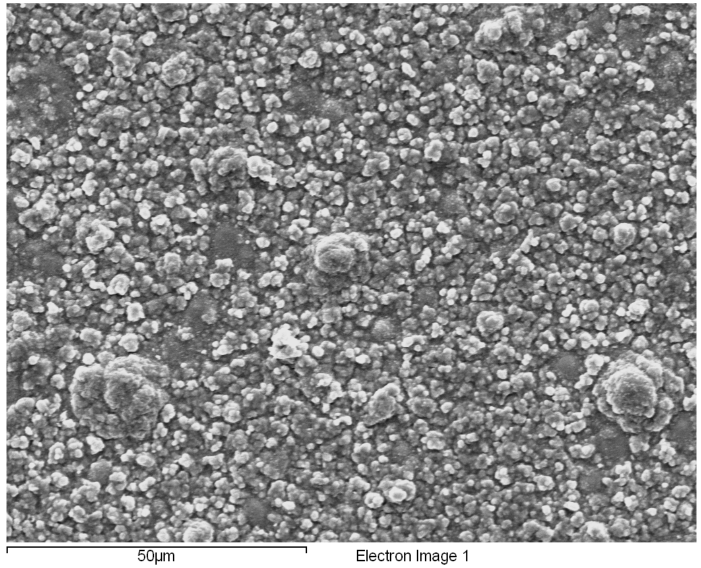


- Reaction in hydride gases (H_2Se, H_2S) or elemental vapors (Se, S): batch or Rapid Thermal Process (RTP)
- Multi-step reaction pathway to form Cu(InGa)Se_2

X-Ray Diffraction Speactra of CIGS Films

XRD, SEM, and EDS characterization on CIGS thin film





- Selenization of CIG precursor film led to the formation of polycrystalline CIGS films with (112) and (220/204) orientations

Sample ID	Process	EDS (at. %)					
		Cu	In	Ga	Se	Cu/III	Ga/III
UA-1	Precursor	39.26	38.09	9.67	-	0.82	0.20
UA-2	H_2Se @450^{o}C 90min	23.66	24.12	1.14	51.09	0.94	0.05

- Low Ga concentration detected by EDS, Ga diffused to CIGS/Mo interface during selenization

Conclusions

- Thermal evaporation of CIGS with CBD CdS developed process produced 10% efficiency devices
- Developed a process to co-sputter CuInGa precursor films within the targeted composition range
- Deposited CuInGa precursors at -35^{o}C substrate temperature which exhibit a dense homogeneous structure with smooth surface morphology
- Investigated the selenization process - Ga diffused to CuInGaSe/Mo interface during selenization