HelioVolt

Application of X-Ray Characterization of In-Situ Growth at NSLS-II to Relevant Manufacturing Process Optimization Issues

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THIN FILM SOLAR SOLUTIONS

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Outline

- Compositional characterization of CIGS
- Synopsis of conventional CIGS synthesis methods
- Reactive Transfer Synthesis (RTS) method of HelioVolt
- Correlation of device performance with coincident XRF and XRD analysis
- Recommendations for further study

Purdue Solar Research Seminar Series

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SYNOPSIS OF CONVENTIONAL CIGS SYNTHESIS METHODS

Characteristics of an Ideal CIGS Manufacturing Method

- High device-quality material
  - Ability to create intrinsic defect structures limiting recombination; role of the order-disorder transition?
  - Ability to control Group III and VI composition gradients
  - Control of extrinsic doping (e.g.: sodium)
- High processing rate
  - Reduces capital cost for targeted throughput
- Low thermal budget
  - Reduces operating cost and energy payback time
- High materials utilization
  - Reduced materials consumption and recycling expenses

Rate Limitations in CIGS Synthesis

- Methods are conventionally categorized as single- or two-stage, but the rate-limiting mechanism is equally important
- Adsorption/Desorption-limited methods
  - Co-evaporation
- Diffusion-limited methods
  - Metal precursor selenization
  - Stacked elemental layer synthesis
- Reaction rate-limited methods
  - Reactive binary alloy precursor synthesis

Synopsis of Prior Art for CIGS Synthesis: Co-evaporation

- First method to achieve 10% efficiency and research approach used to make all record cells since 1989
- Simultaneous evaporation of the constituent elements onto a high-temperature (450-700°C) substrate to directly synthesize CIGS in a single stage process
- Competition between adsorption and desorption kinetics reduces (1) selenium utilization and (2) indium incorporation at temperatures near/above the order-disorder transition
- Extended dwell at high temperatures generates high thermal budget and equipment costs

Synopsis of Prior Art for CIGS Synthesis: Metal Precursor Selenization

- Most well-developed, widely used approach for commercial manufacture of CIGS modules, providing good large-area uniformity
- Deposition of multilayer metal films by PVD, plating, or particle suspensions followed by second-stage high-temperature annealing in Se or H_2Se/H_2S
- Complex intermetallic alloying reactions and differential diffusion during selenization cause uncontrolled segregation
- Selenium/Sulfur diffusion limits reaction rate and resulting extended dwell at high temperature generates high thermal budget; first stage deposition method determines materials utilization efficiency and capital intensity

Synopsis of Prior Art for CIGS Synthesis: Stacked Elemental Layers (SEL)

- Differs from the metal selenization approaches by incorporating layers of selenium, as well as the metals, into the precursor film itself
  - Circumvent the need to diffuse selenium through the entire thickness of the precursor stack
  - Enables intervention in intermetallic formation by stacking sequence control
  - Multi-step reaction kinetics shown to generate compound intermediates prior to CIGS formation
- Rapid thermal processing used in second stage to minimize thermal budget and parasitic reactions

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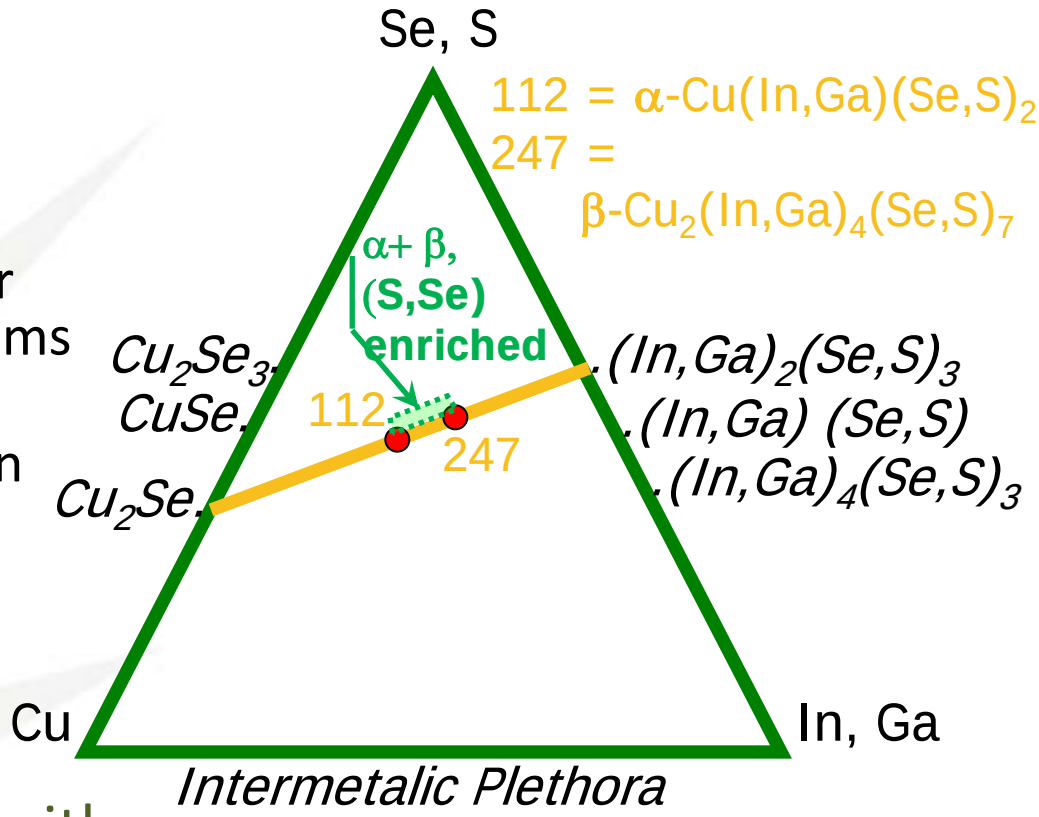
REACTIVE TRANSFER SYNTHESIS: RTS

Reactive Transfer Synthesis of CIGS from Compound Precursors

- Two-stage process
  1. Low-temperature deposition of multilayer compound precursor films
  2. Rapid reaction of compound precursors in chalcogenide vapor including condensation *via* vapor sublimation to form CIGSS
- Combines reactive binary alloy precursor synthesis with CSVT for surface modification



Reactive Transfer Synthesis (RTS)

- Stage 1: Precursor Deposition
  - Low-temperature Vacuum Co-evaporation
    - Equipment requirements similar to conventional single-stage co-evaporation but lower temperatures lead to higher throughput and reduced thermal budget
- Stage 2: Reaction
  - Rapid processing of multilayer compound precursor film in chalcogenide vapor. Can be combined with proximity cap Close-Spaced Vapor Transport (CSVT) to modify near-surface composition.

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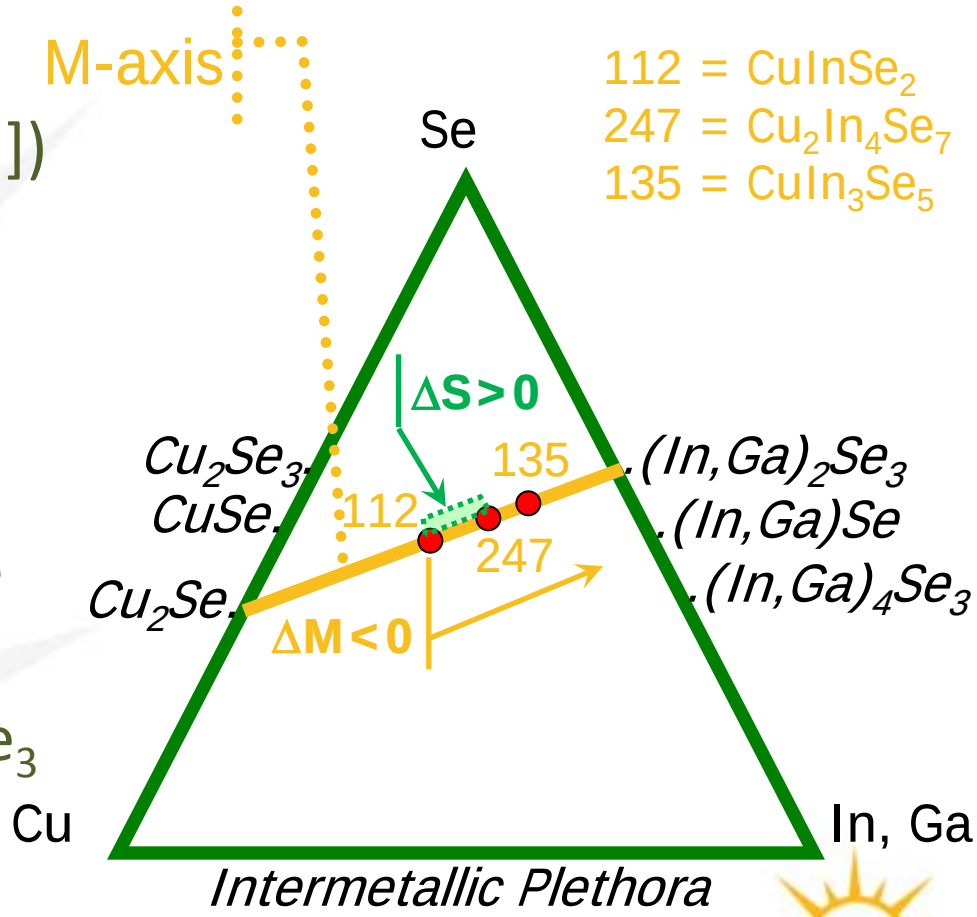
XRF COMPOSITIONAL CHARACTERIZATION OF CIGS

Cu–(In,Ga)–Se Ternary Alloys Molecularity (M) and Stoichiometry (S)

- M= [Cu]/([In]+[Ga])
- S = 2[Se]/[Cu]+3([In]+[Ga])
- ΔM= M-1; ΔS= S-1
- ALL **high-efficiency CIGS devices have** ΔM<0 and ΔS>0
- Formation reaction; note M = $y/(1-y)$:

  $y\,Cu_2Se + (1-y)\,(In,Ga)_2Se_3 + \Delta Se \rightarrow (Cu_y(In,Ga)_{1-y})_2Se_{3-2y+\Delta Se}$



CIGS Alloy Non-Stoichiometric Thermochemical Phase Structure

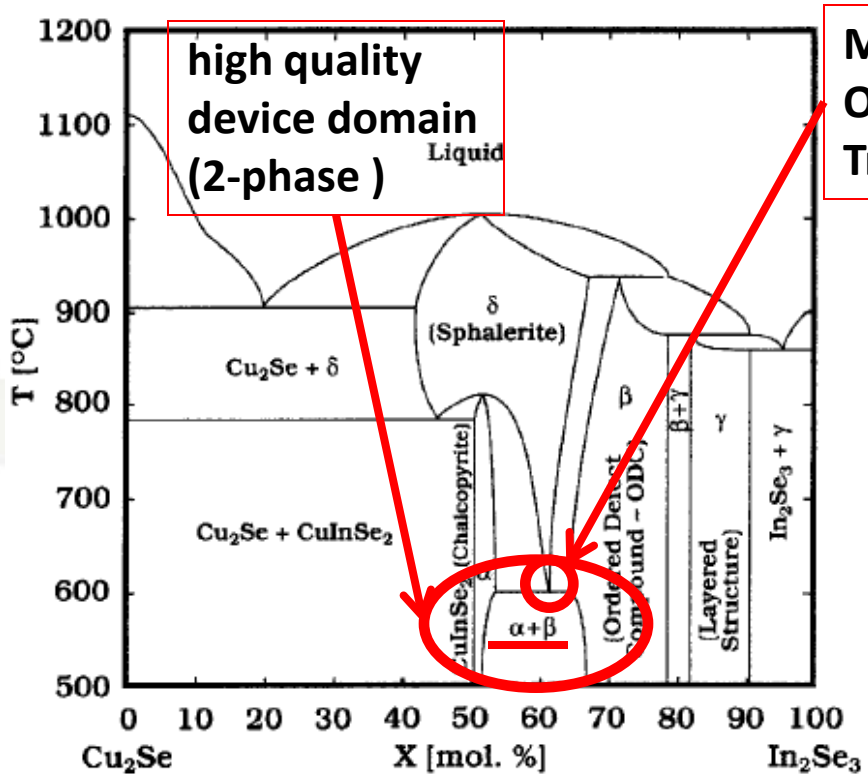


FIGURE 1. Adapted from a published assessment of the phase diagram along the Cu_2Se – In_2Se_3 pseudobinary section of the Cu–In–Se chemical system.[33]

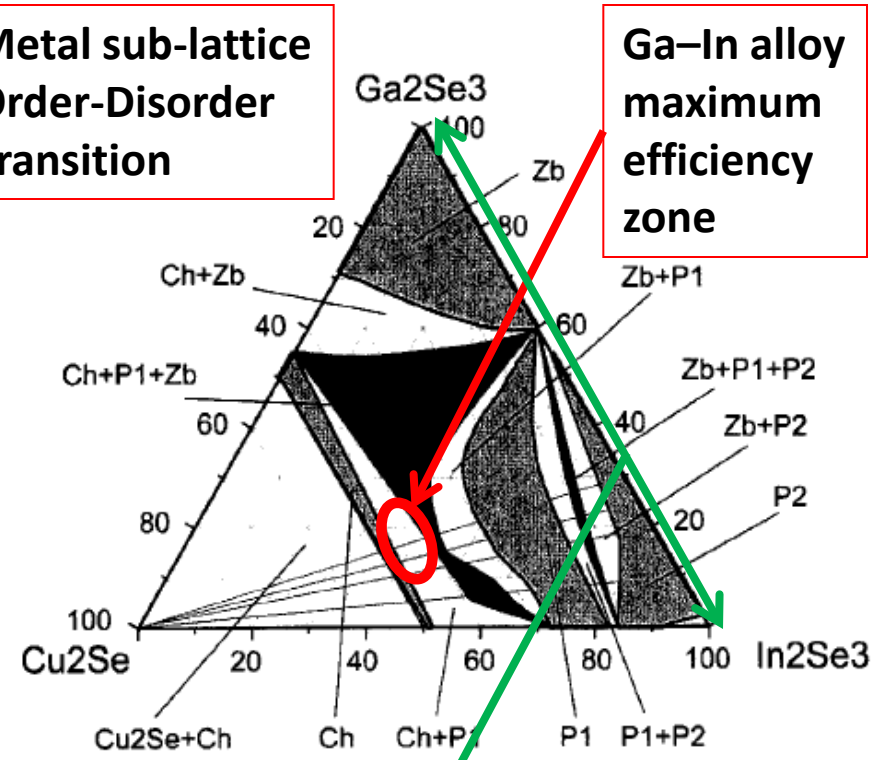


FIGURE 4. Predominance diagram for the Cu_2Se–In_2Se_3–Ga_2Se_3 pseudoternary phase field at room temperature.[135] In that author's notation, Ch is the α phase, P1 is the β phase, P2 is the γ phase, and Zb is the δ phase.

- Gallium fraction = [Ga]/([Ga]+[In])

CIGS Composition Variables Used for XRF Characterization Analysis

- XRF is widely used by industry to monitor and control composition of CIGS alloy films
  - Copper ratio (molecularity variable M)
  - Gallium ratio (CGS alloy fraction)
  - Selenium ratio (stoichiometry variable S)
    - XRF is of limited usefulness for selenium except excessive $MoSe_2$ formation yields anomalously high values
- XRF does not provide profile information for non-uniform depth profiles and tends to overweight the surface composition, albeit not as much as EDS

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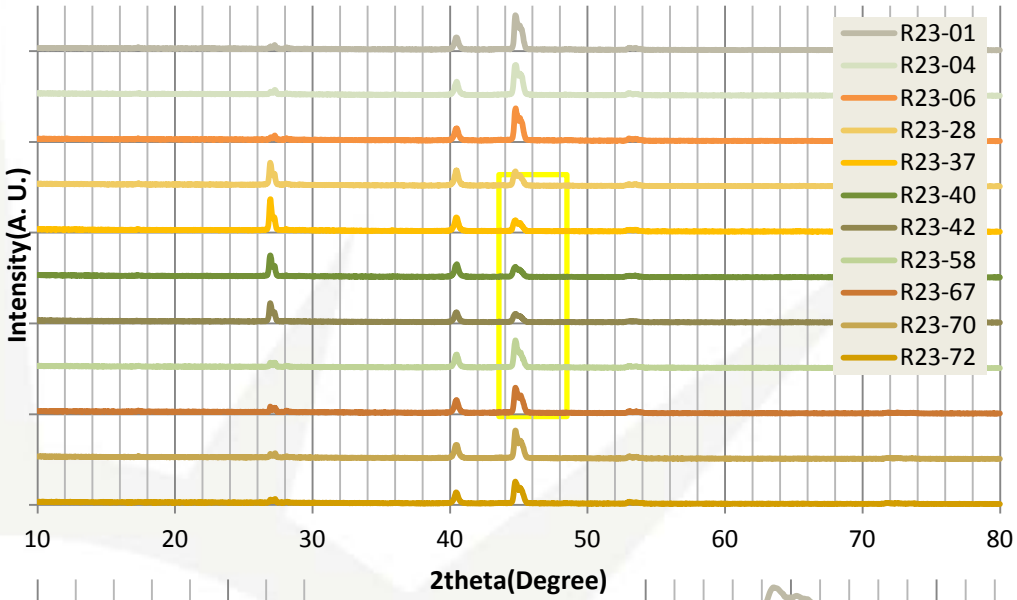
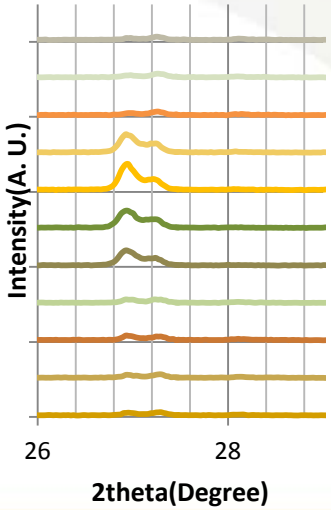
XRD CHARACTERIZATION OF CIGS USED IN INDUSTRY

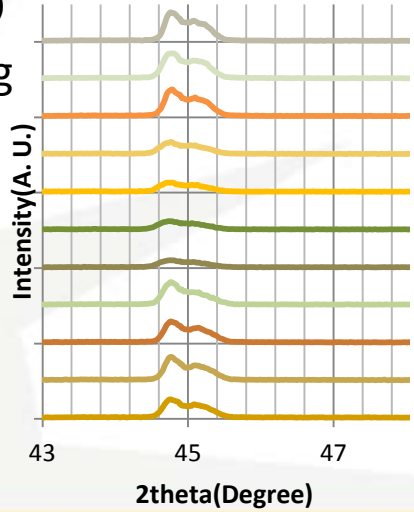
Exemplary XRD-Eff data

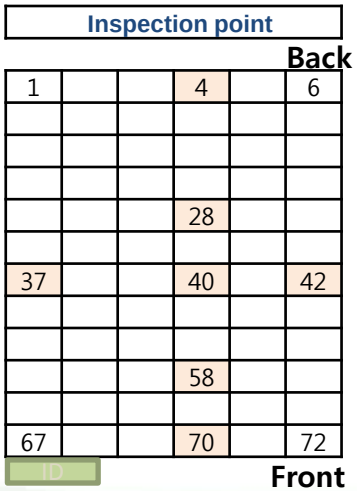


efficiency	Sample No.	Cu ratio	Ga ratio	Thickness(um)
13.68	1	0.81	0.34	1.43
12.94	4	0.80	0.33	1.53
12.69	6	0.78	0.33	1.56
12.40	28	0.81	0.33	1.52
13.22	37	0.86	0.32	1.31
12.70	40	0.85	0.31	1.36
14.14	42	0.84	0.32	1.30
13.57	58	0.81	0.32	1.54
9.60	67	0.80	0.33	1.43
9.50	70	0.78	0.33	1.56
10.75	72	0.78	0.33	1.54



Peak-splitting due to graded Ga-ratio used to grade bandgap structure?





Quantitative Analysis of Texturing Using Normalized Peak Ratio (NPR)

- HelioVolt relies extensively on statistical methods for both the design of experiments (DOE) and analysis of data
- Quantification of θ–2θ XRD scan data is conducted by:
  - Measuring the peak amplitude of the [220]/[204] (~27°) and [112] (~45°) peaks and compute their ratio
  - Computing the same ratio for the powder diffraction JCPDS files corresponding to CIGS
  - Calculating the ratio of these ratios (measured/JCPDS), which we refer to as the **Normalized Peak Ratio (NPR)**

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PV DEVICE PERFORMANCE/XRF-XRD CORRELATION ANALYSIS

Industrial CIGS Manufacturing and Large-Area Uniformity Imperative

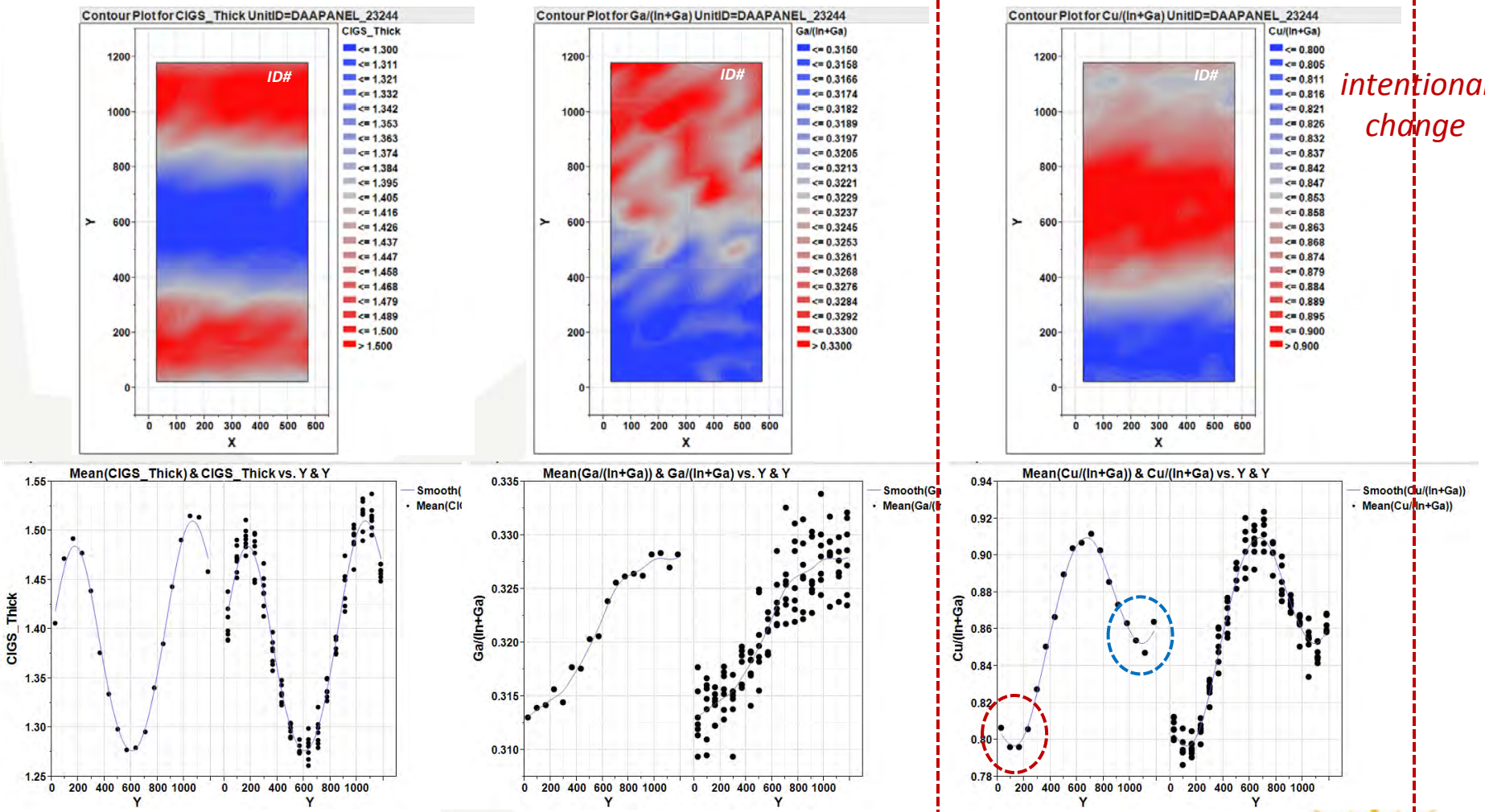
- GW-scale PV manufacturing requires output of thousands of square kilometers
- Two basic approaches are used by industry to employ thin-film CIGS cells in modules:
  - Monolithic integration on glass/polymer dielectric
  - Assembly of individual cells deposited on metal foil
- Both methods require large-area uniformity in order to achieve high yield and high efficiency of module comprised of series-connected cells
  - Dispersion of cell JV characteristics must be minimized for cost-effective manufacturing

Intentional Cu-Ratio Gradient Formation

THK=1.41±0.10µ

GaR=0.32±0.01

CuR=0.86±0.06



intentional change

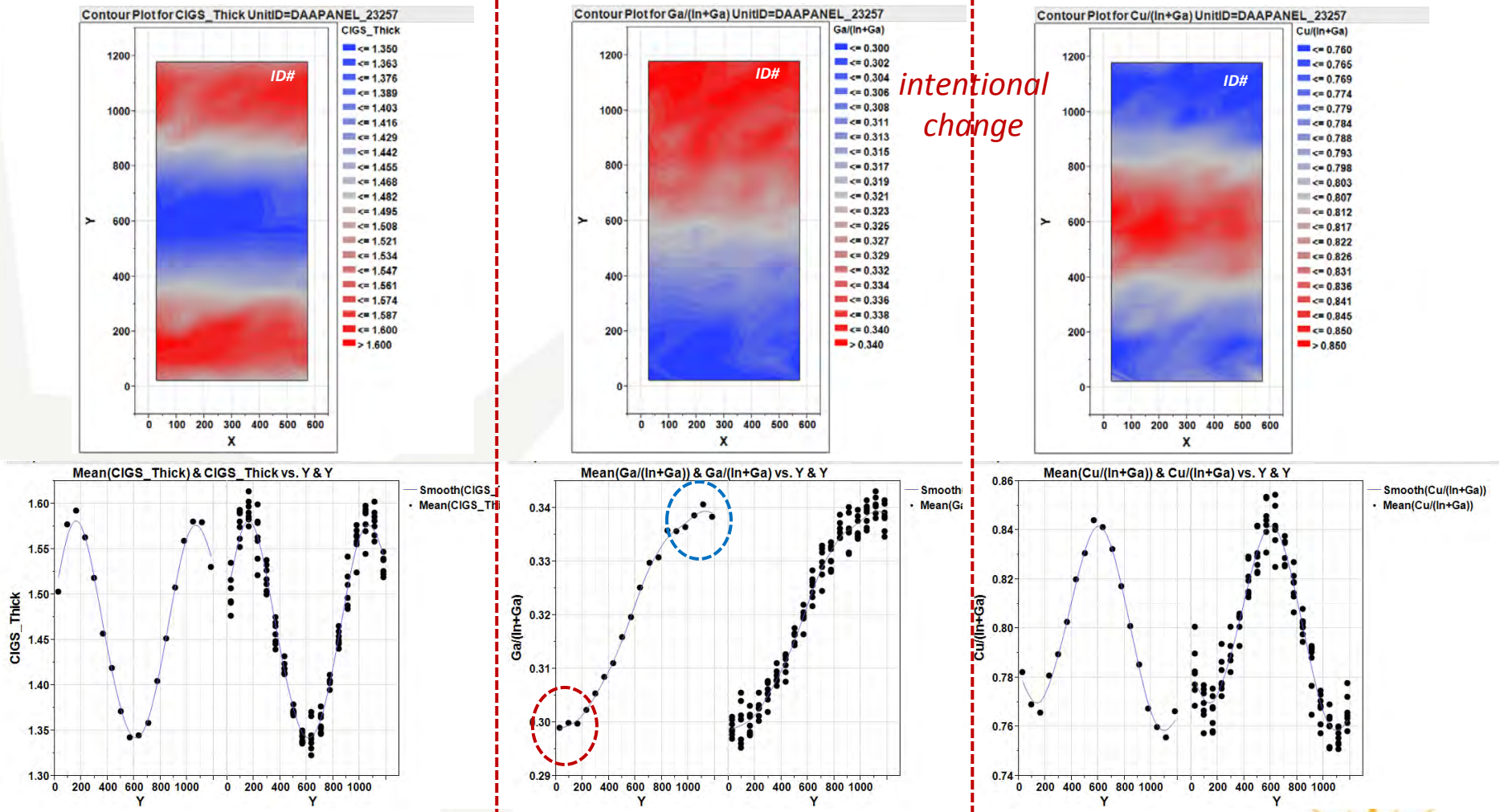
- Intentional Cu-ratio manipulation yields weak Ga-ratio gradient

Intentional Ga-Ratio Gradient Formation

THK=1.48±0.10µ

GaR=0.32±0.02

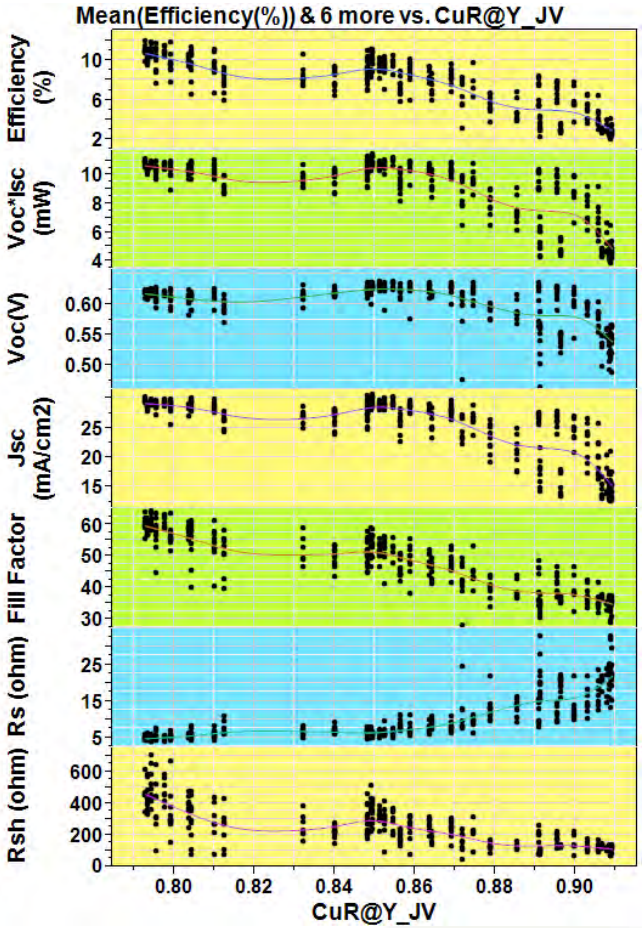
CuR=0.80±0.03



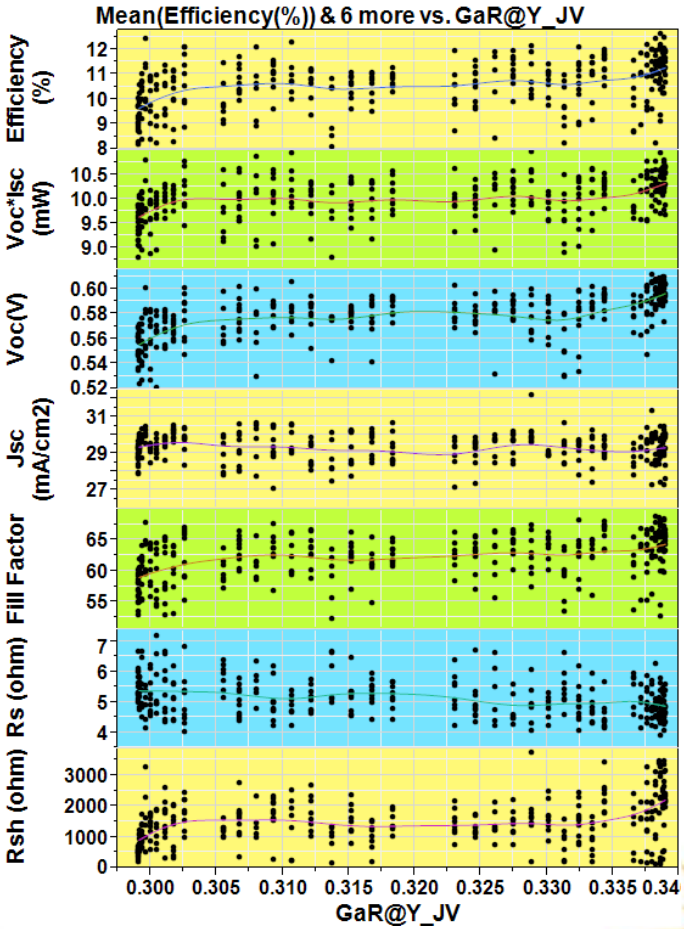
- Intentional Cu-ratio manipulation yields weak Ga-ratio gradient

Cell Efficiency*-Composition Correlation

Rapid Efficiency loss when CuR>0.85



Weak but significant improvement with higher GaR in 0.30-0.34 range



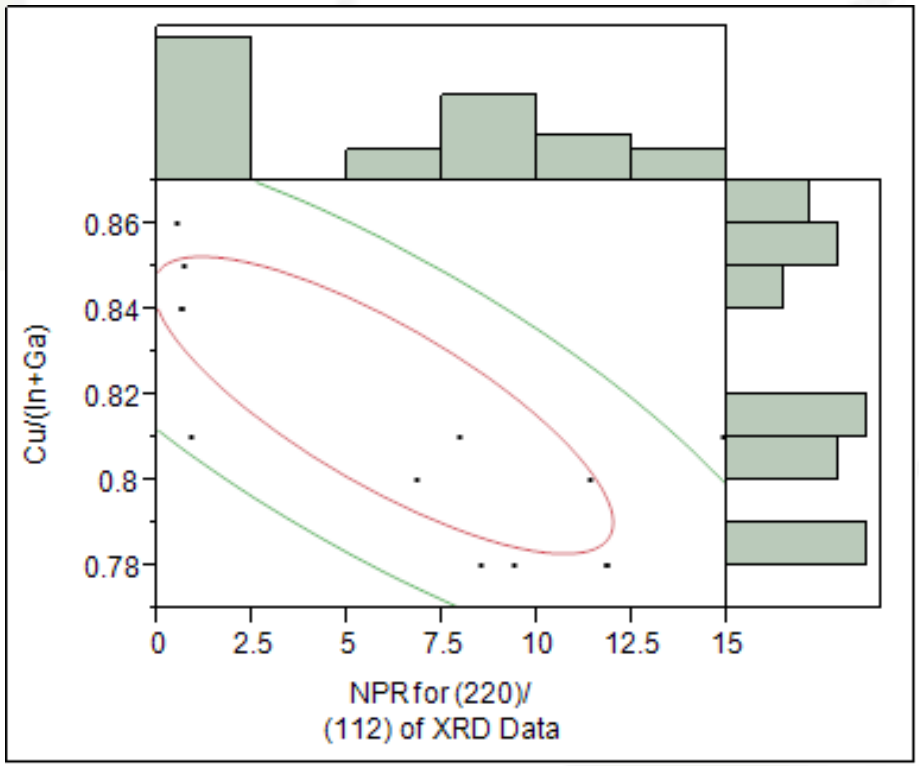
*Note cells are neither light-soaked (low Voc) nor AR-coated (low Isc)

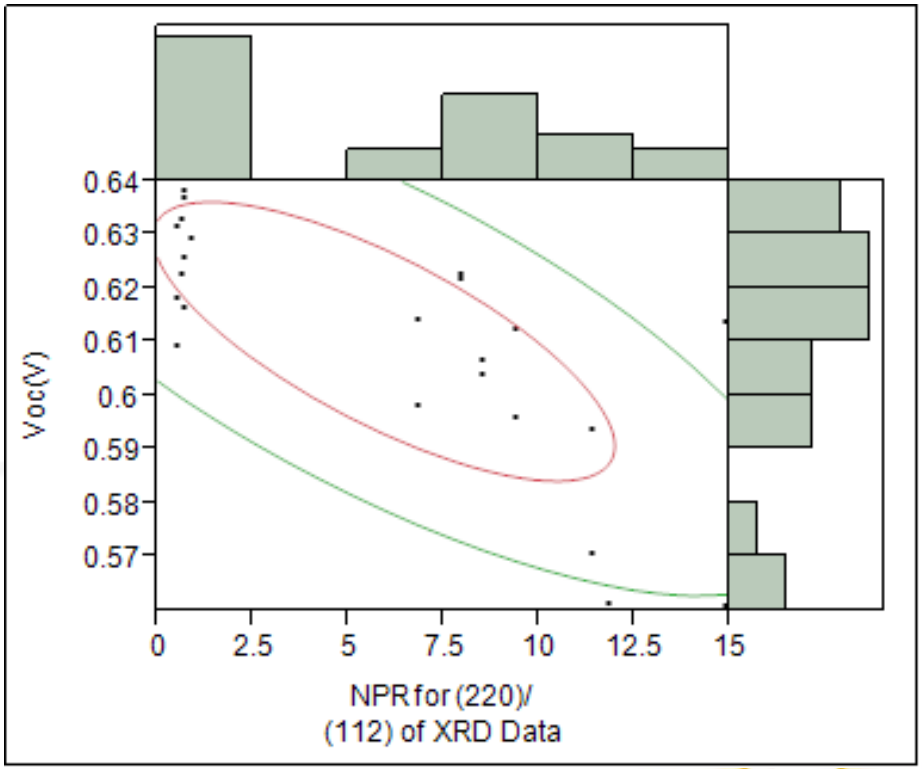
XRF Composition-XRD NPR Correlation with V_{OC}

Strong Correlation Between Higher Cu-Ratio and [112]/Random Orientation Observed

Correlation Between Voc and NPR also Strong:

So which if either is causal?



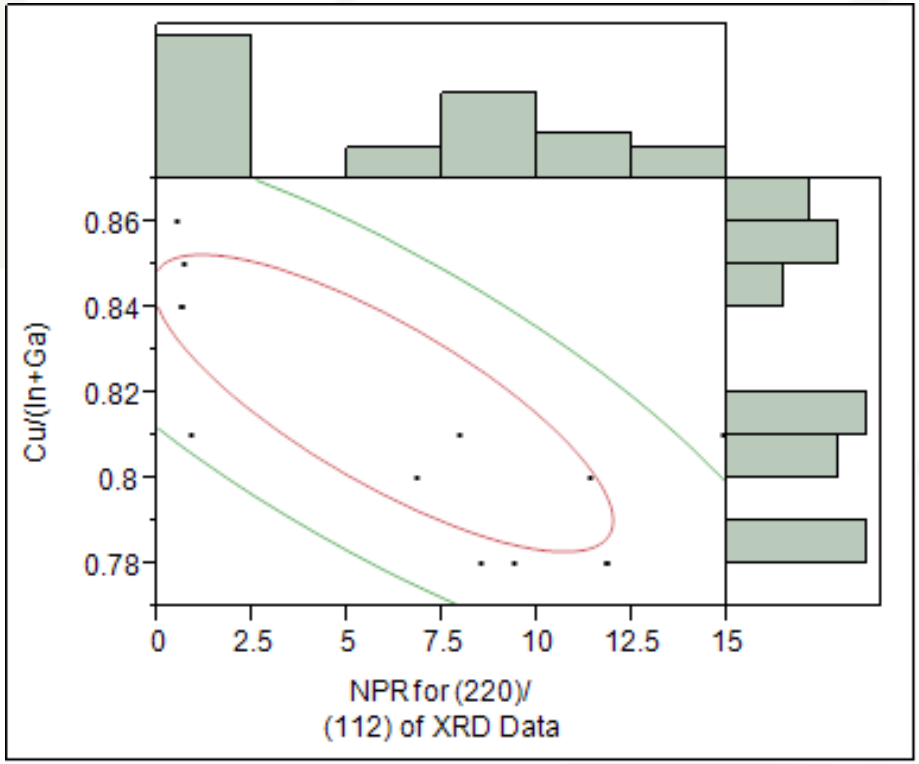


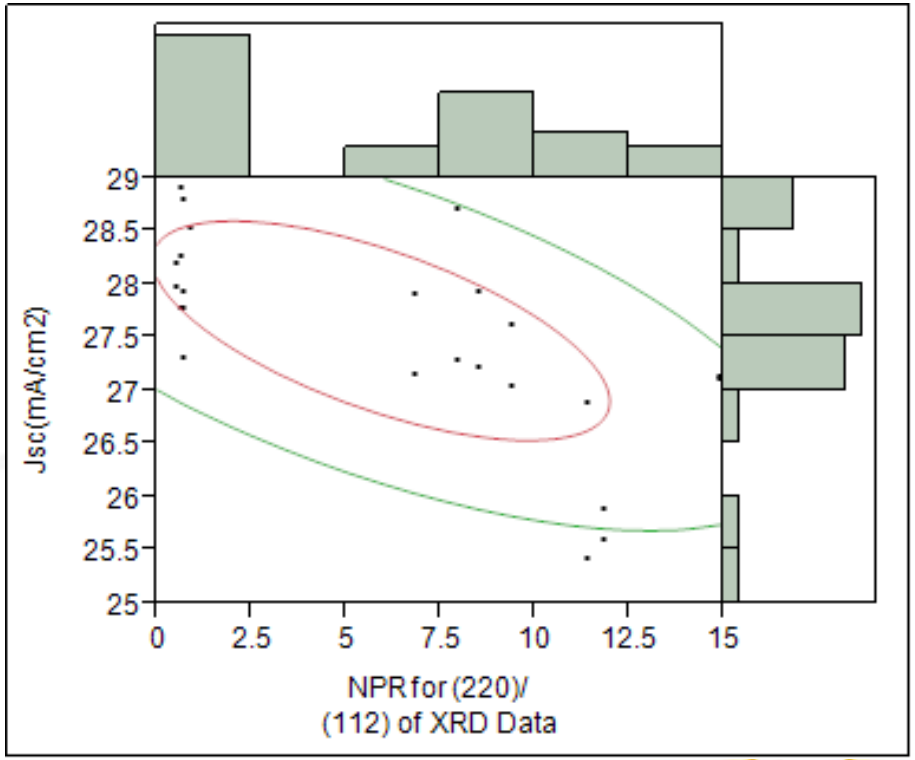
XRF Composition-XRD NPR Correlation with I_{SC}

Strong Correlation Between Higher Cu-Ratio and [112]/Random Orientation Observed

Correlation Between Voc and NPR also Strong:

So which if either is causal?





Similarity between Co-evaporation and RTS Methods Relevant to Crystallography

- Both methods rely on the initial deposition of $(In,Ga)_2Se_3$ onto Mo-coated glass, followed by topotactic transformation to CIGS by reaction with Cu_XSe
  - Orientation of CIGS controlled by that of initial IGS
  - Studies have shown that CIGS orientation influenced by numerous factors in co-evaporation processes
    - Higher Se/Metal flux ratios increase [220]/[204] texturing(1)
    - Excessive Na availability and no Na both lead to preferred [112] texturing(1)
    - Molybdenum orientation can effect CIGS orientation(2)

(1) G. Hanna, et al, Thin Solid Films, v. 431–432 (2003) pp. 31-36
(2) T. Schlenker, et al, Thin Solid Films, v. 480–481 (2005) pp. 29-32

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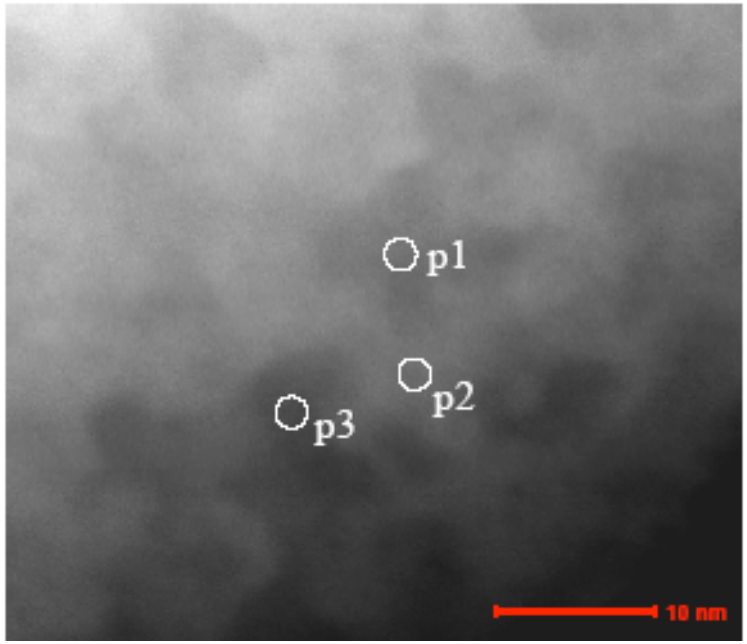
CHALLENGES AND OPPORTUNITIES FOR INDUSTRIALLY-RELEVANT RESEARCH USING *in situ* X-RAY PROBES

Composition Fluctuations and Carrier Transport in CIGS PV Absorbers

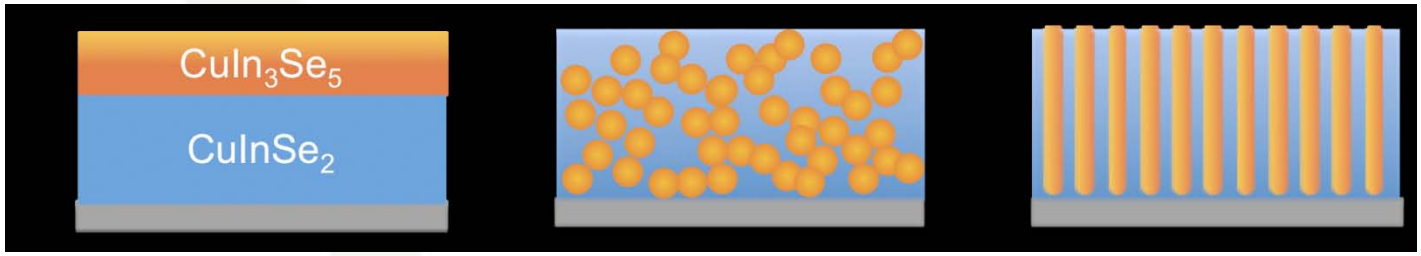
- Theoretical model *a priori* predicted preferential Ga-In distribution between segregated phases
- Experimental results* HAADF-TEM & nano-EDS
  - 5-10 nm characteristic domain size (2-D)
  - Pearson product-moment statistical correlation between the two variables Cu/(In+Ga) and Ga/(In+Ga) is 0.72 (null P=0.3%)



*Applied Physics Letters, 87, 2005, 121904

Role of Nano-Engineering in Next-Generation CIGS PV Device Technology

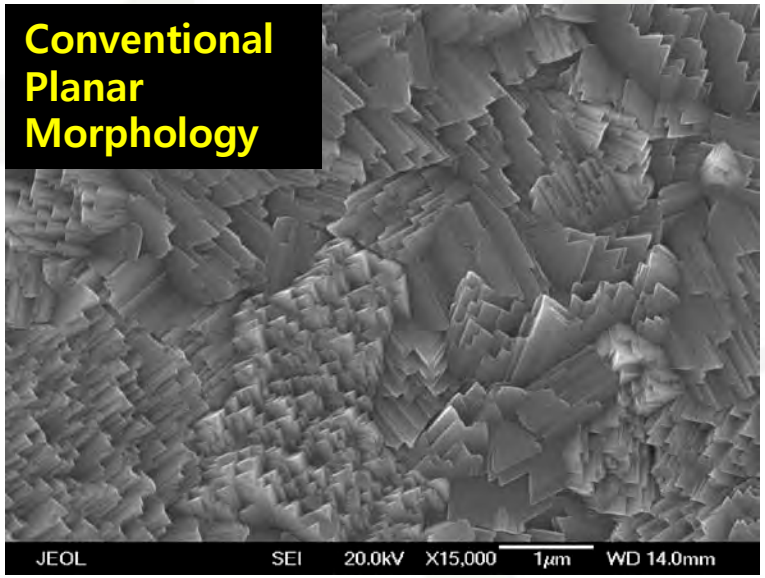
- Intra-Absorber Junction (IAJ) model
  - Device-quality CIGS is a two-phase mixture of *p*-type α-CIGS and *n*-type β-CIGS phases, forming a nanoscale bulk heterojunction.
  - These internal junctions form an interpenetrating percolation network, allowing positive and negative charges to travel to the contacts in physically separated paths, reducing recombination.
- Presents opportunity for optimization of nanostructures in CIGS by engineered nanostructure synthesis
  - HelioVolt has large IP portfolio of relevant patents both issued and pending, including use of anisotropic nanostructures

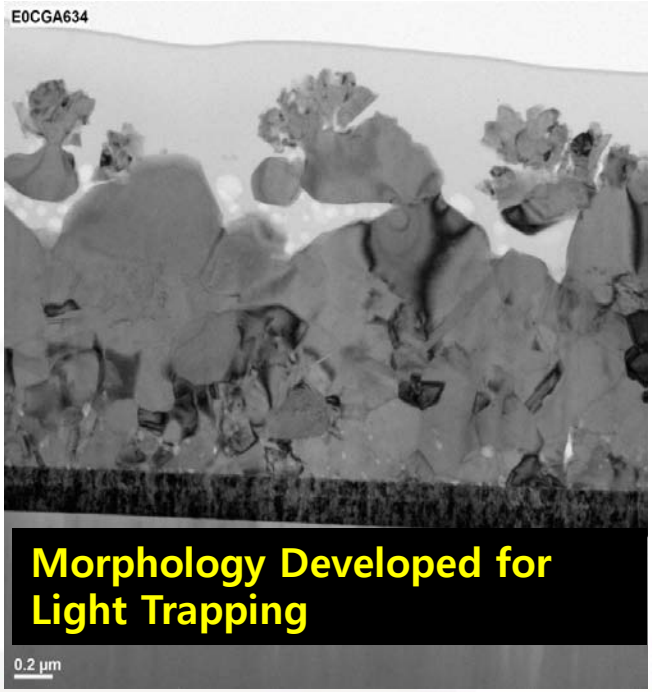


•single heterojunction between Cu-rich and Cu-deficient phases,
•randomly oriented bulk heterojunction formed by spontaneous nucleation, and
•an ideal vertically oriented bulk heterojunction.

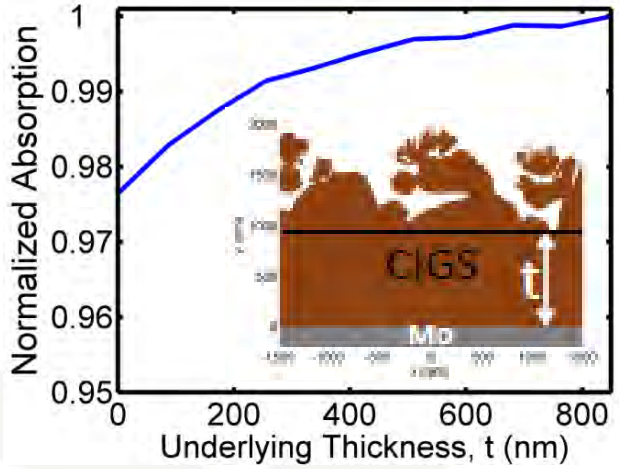
Self-Assembled Nanostructure Formation for Enhanced Light Trapping

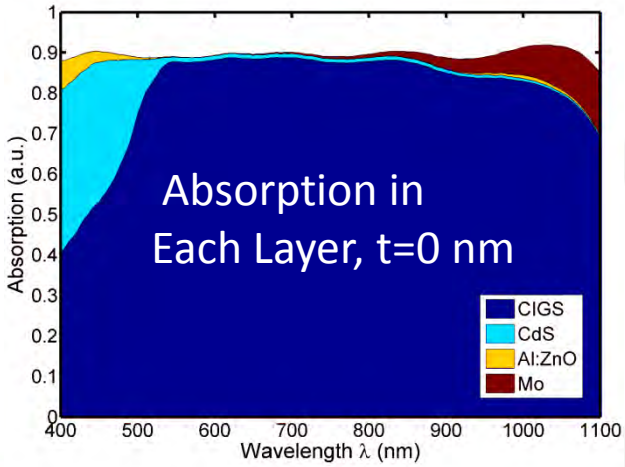
- Precursor deposition and reaction processes can been optimized to induce formation of mesoscale morphological asymmetries in the final structure by Cu-Se flux-assisted re-crystallization characterized by coalescence and coarsening of both the CIGS grains and the voids formed between them by reactive mass transport





Impact of CIGS Thickness Reduction on Nanostructure's Solar Absorption





- Microstructure reduces reflection better than an ideal 2-layer ARC on planar absorbers
- Maximum possible J_{sc} for t= 0 nm is 38.24 mA/cm_2 compared with 37.61 mA/cm_2 with ARC on planar absorber over AM1.5G solar spectrum (E_g=1.15eV)
- Reflection from planar ZnO dominant; absorption in bulk negligible (2% relative)
- Flat character of CIGS absorption below CdS band-edge matches measured EQE well

Challenges

- A wide breadth of research has shown that composition fluctuations within CIGS limit its performance, but may also be one root cause of its defect tolerance.
  - A better understanding of this may be essential to achieving CIGS efficiencies closer to the Shockley-Queisser limit
- Fundamental studies of the crystallographic orientation dependence of relative rates of indium and gallium diffusion into Cu_XSe have never been conducted.
  - Observed performance differences with orientation may be caused by subtle differences in resulting bandgap profiles
  - Control of differential group III segregation important to optimization of both planar and nanostructured CIGS

Thank You!

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