Cryogenic cathodoluminescence of $Cu_xAg_{1-x}InSe_2$ thin films

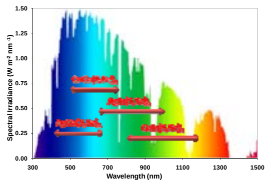
Angel R. Aquino[1], Angus A. Rockett[1], Scott A. Little[2], Sylvain Marsillac[2]

[1]*Department of Materials Science & Engineering, University of Illinois, Urbana Illinois USA*

[2]*Wright Center for Photovoltaics Innovation and Commercialization, University of Toledo, Toledo Ohio USA*

Motivation

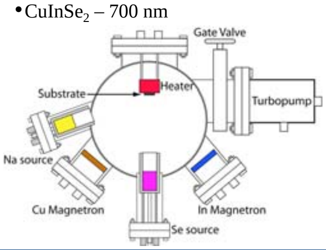
- Cu(In,Ga)Se_2 is leading choice for high performance thin film solar cells (20.1% efficiency)
- Bandgaps of the I-III-VI_2 system (I-Cu,Ag; III-Ga,In; VI-S,Se) cover almost the entire solar spectrum, which make it an ideal system for multijunction solar cells
- However, these make poor solar cells because most of their properties, including recombination mechanisms, are poorly understood
- Cathodoluminescence (CL) offers simultaneous scanning of electron and spectroscopic images
- Our goals are to:
  - Study luminescence behavior close to grain boundaries
  - Identify emission differences between samples (Cu vs Ag)
  - Characterize emissions and possible defects responsible for transitions
- First report of cryogenic CL with spectral imaging on $AgInSe_2$ and $Cu_xAg_{1-x}InSe_2$



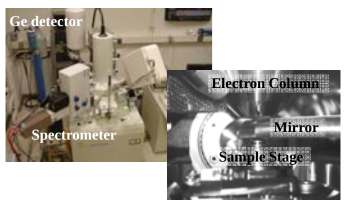
Experimental Setup

Thin film deposition system

- Hybrid sputtering/evaporation
  - Sputtering of metals (Cu, Ag, In)
- Substrate held at 550°C
- Three films analyzed
  - $AgInSe_2$ – 300 nm
  - $Cu_{0.6}Ag_{0.4}InSe_2$ – 700 nm
  - $CuInSe_2$ – 700 nm



JEOL 7000F analytical SEM

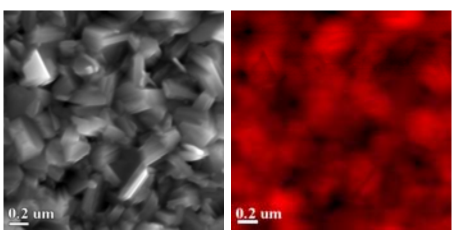


- Gatan MonoCL3 Spectrometer
- Liquid N_2-cooled Ge detector
- Liquid He-cooled stage module
- Sample temperature ~ 5K
- Accelerating Voltage = 15 kV
- Current varied from 22 pA-160,000 pA
- Some samples were carbon coated to avoid charging during imaging

Panchromatic CL Imaging

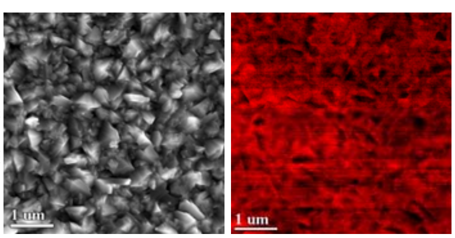
SEM Images | PanCL Images | Observations

$AgInSe_2$



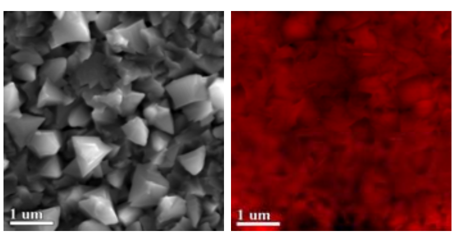
- Very spatially **uniform emissions**
- Most **dark areas** in **PanCL** image correspond to **dark areas** in the **SEM** image
- Very few grains show reduced emission intensity from facets
- **No reduction in emission intensity from protuberant surface features**

$Cu_{0.6}Ag_{0.4}InSe_2$



- Much **more spatial variation** of emissions
- **Dark areas** in **PanCL** image correspond to **bright areas** in **SEM** image
- Severe reduction in emission intensity seen from protuberant surface features
- Very **intense emissions** coming from **areas in between grains** (dark areas in SEM image)
- Local variations in luminescence are indicative of local variation in defect states or composition

$CuInSe_2$

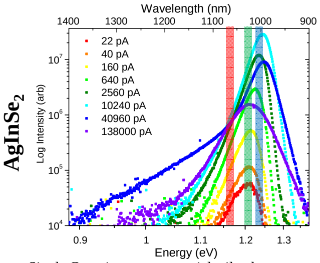


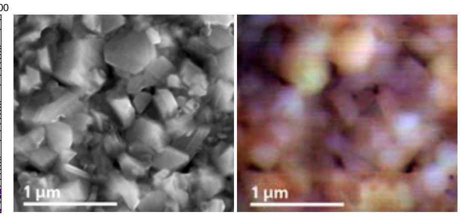
- More spatial variation of emissions than in pure $AgInSe_2$, but less than in $Cu_{0.6}Ag_{0.4}InSe_2$
- **Reduction in emission intensity** seen as we **approach surface facets or grain edges**
- Center of grains luminesce very well
- **Intense emissions** seen **around grains**

Power-series and Spectral Imaging

Power-dependent Spectra | **SEM Images** | **Monochromatic CL Overlay**

$AgInSe_2$



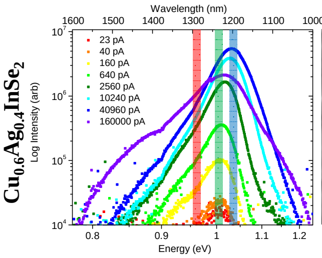


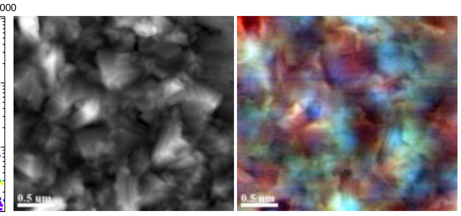
= 1010 nm = 1020 nm = 1060 nm

- Single Gaussian + exponential tail at low excitation power
- At excitation powers above 2560 pA we see new exponential tails at both the high and low energy ends
- Blue shift of main Gaussian peak

- Aligned and overlaid spectral images show **spatial and spectral uniformity**
- No enhanced emission from grain boundaries or inter-grain areas
- **Uniformity in emission indicates compositional uniformity**

$Cu_{0.6}Ag_{0.4}InSe_2$



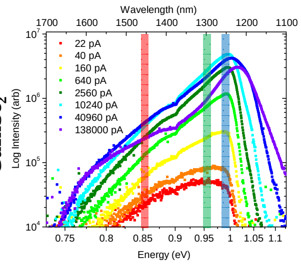


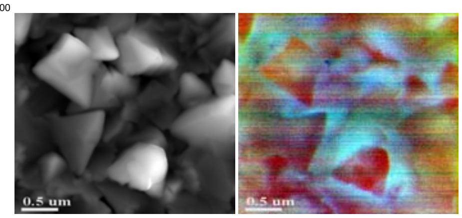
= 1200 nm = 1230 nm = 1280 nm

- Two Gaussians at low excitation power
- Low and high energy end exponential tails appear at higher excitation powers together with additional Gaussian
- Blue shift of Gaussian peaks

- Aligned and overlaid spectral images show **spatial and spectral variation**
- Enhanced emission from grain boundaries and inter-grain areas
- **CAIS has the most variation of emissions from grain to grain, indicating compositional fluctuations between grains**

$CuInSe_2$





= 1260 nm = 1300 nm = 1450 nm

- Very broad emission requires 4+ peaks to fit + exponential tail at low energy
- High energy (1200 nm) Gaussian starts emitting above 640 pA
- Blue shift of main Gaussian peaks

- Aligned and overlaid spectral images show **spatial and spectral variation**
- Red emission, although very uniform, is most intense inside grains even close to facets and surface features
- Green and blue emissions strongest from grain boundaries and inter-grain areas
- **CIS has most emission variation from grain to boundary indicating compositional fluctuation between grain and grain boundaries**

Conclusions

- Emissions from **$AgInSe_2$** are **more uniform** both spatially and spectrally than Cu-containing samples
- $AgInSe_2$ less affected by reduced emission from surface features – partly due to less surface faceting
- **Cu-containing samples** exhibit **enhanced luminescence** from **grain boundary** or inter-grain areas
- Both **Cu-containing samples exhibit localized luminescent variations** indicative of **compositional fluctuations** or **electrically active defect fluctuations**
- **As Cu increases, emission gets broader** indicating larger number of specific defect states (more local chemical variation)
- **Device implications: AIS** may produce **more uniform cell performance** and may exhibit **less air-sensitivity** during manufacture

Acknowledgments

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ILLINOIS

Scan with smartphone for author's contact info

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WRIGHT CENTER for PHOTOVOLTAICS INNOVATION AND COMMERCIALIZATION

THE UNIVERSITY OF TOLEDO 1872