# *Effects of Alkali-PDT on Low Bandgap $(Ag,Cu)InSe_2$ Solar Cells*

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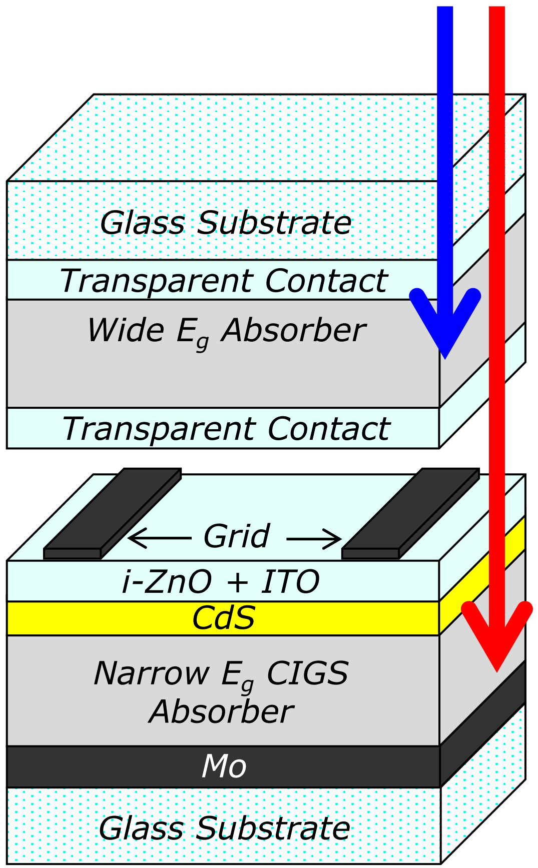
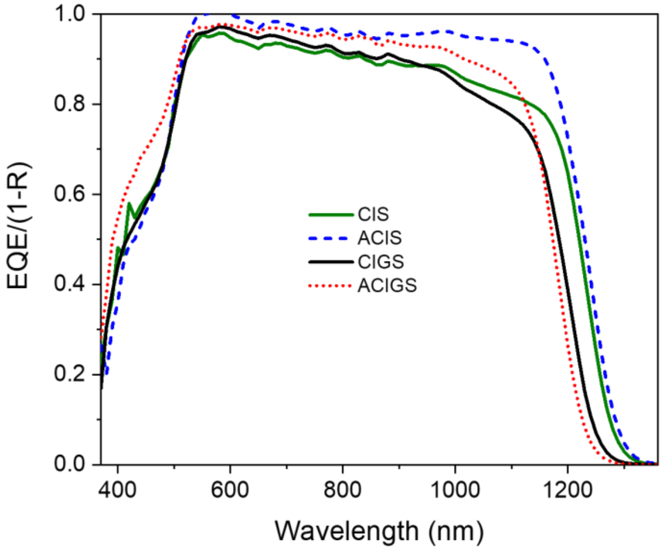
# Motivation

- Interest in CIGS to be a bottom cell in a tandem
- Reduced Ga/(Ga+In) (GGI) is required to lower the bandgap ($E_g$)
  - But lower efficiencies obtained with $E_g$ < 1.1 eV
- What approaches will improve efficiency of low $E_g$ CIGS?



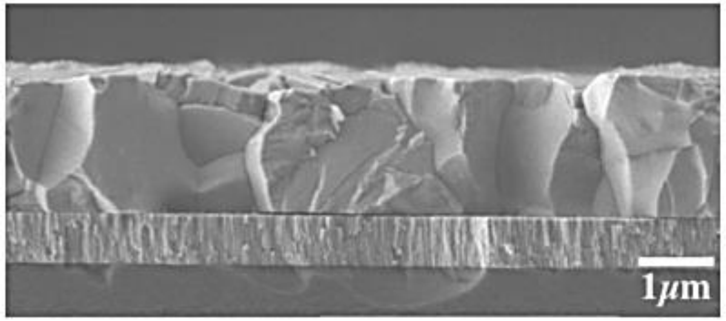
# Approach 1: Ag Alloying

- Lower defect density (Erslev et al. 2011)
- Longer minority carrier lifetime (Garris et al. 2017)
- Larger grain sizes (Chen et al. 2014)
- Improved long wavelength QE in low $E_g$ devices (Valdes et al. 2019)

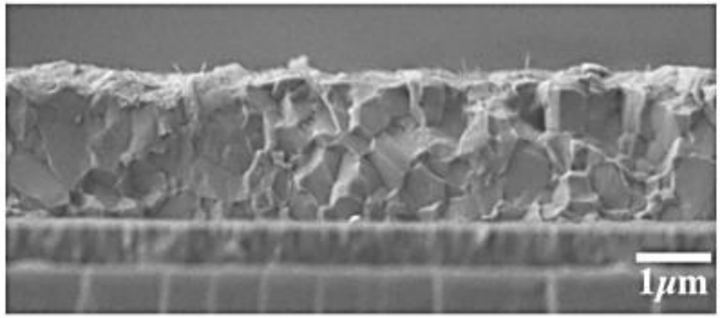



N. Valdes et al., *Sol. En. Mater. Sol. Cells*, 2019.

ACIGS




CIGS




L. Chen et al., *IEEE J. Photovoltaics*, 2014.

# Approach 2: Alkali Post-Deposition Treatments

- Led to record efficiency CIGS solar cells
- Most PDT studies done on co-evaporated CIGS, with GGI = 0.2 – 0.4
  - We've focused on:
    - Will the PDT results apply for GGI = 0 (CIS)?
    - The effect of Ag on PDT – for interest in Ag alloyed CIS and CIGS

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rrl solar

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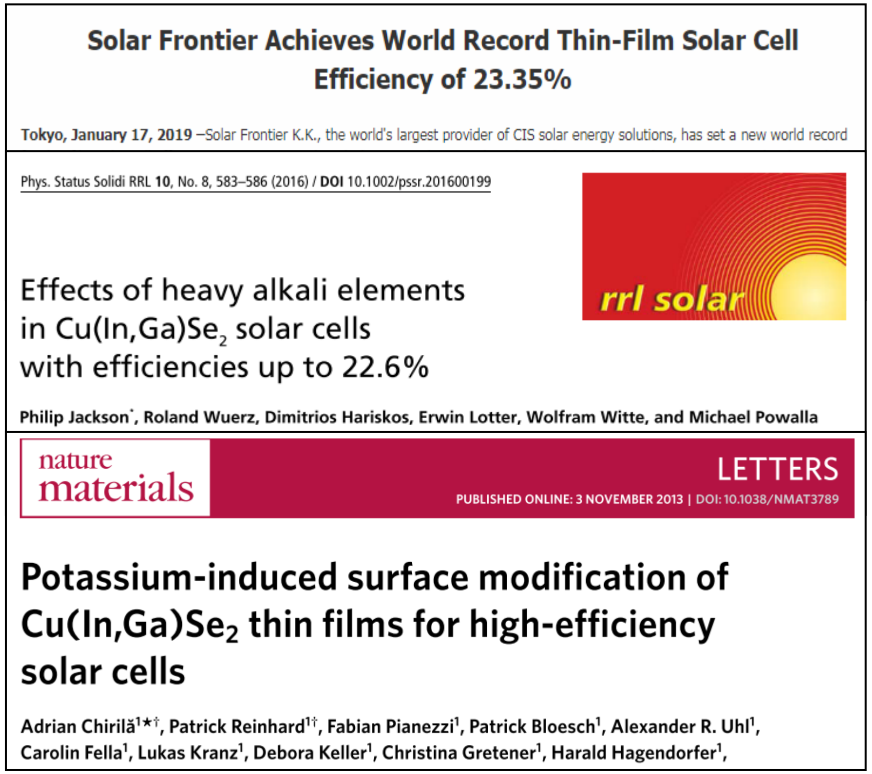

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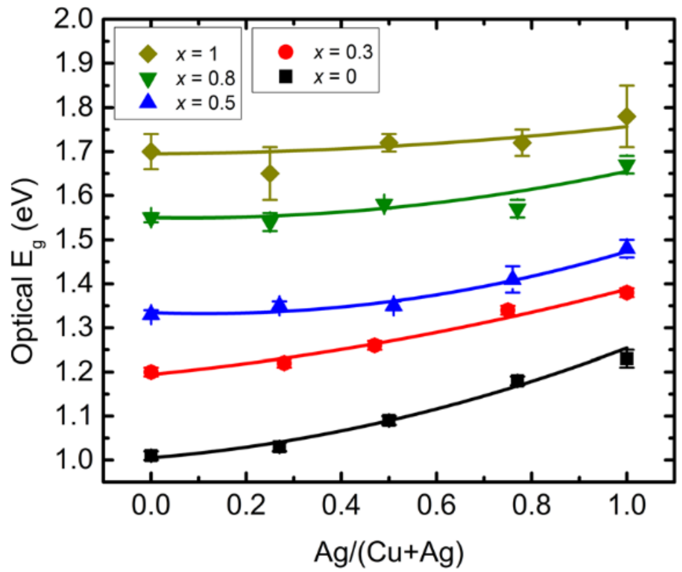
How do Ga and Ag influence the alkali-PDT on $CuInSe_2$?

# Experimental Details

- Use three-stage co-evaporation to grow the following absorber layers:
  - CIS
  - CIGS
  - ACIS
- Composition and thickness by x-ray fluorescence (XRF):
  - GGI = 0 or 0.3
  - Ag/(Ag+Cu) = 0 or 0.2 (minor influence on $E_g$)
  - (Ag+Cu)/(In+Ga) = 0.85
  - Thickness = 2.5 – 3 µm

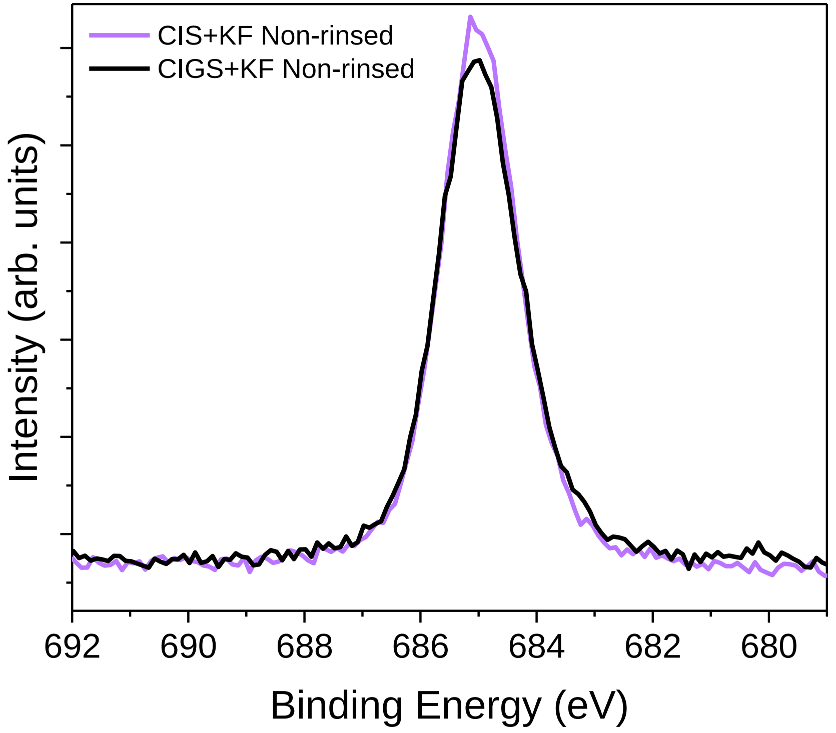



J. Boyle et al., *J. Appl. Phys.*, 2014.

- Samples with alkali-PDT: ~7.5 nm KF or RbF with $T_{sub}$ = 350°C with Se flux
  - Compare samples rinsed vs. not rinsed with deionized water

How does Ga influence the KF-PDT on $CuInSe_2$?

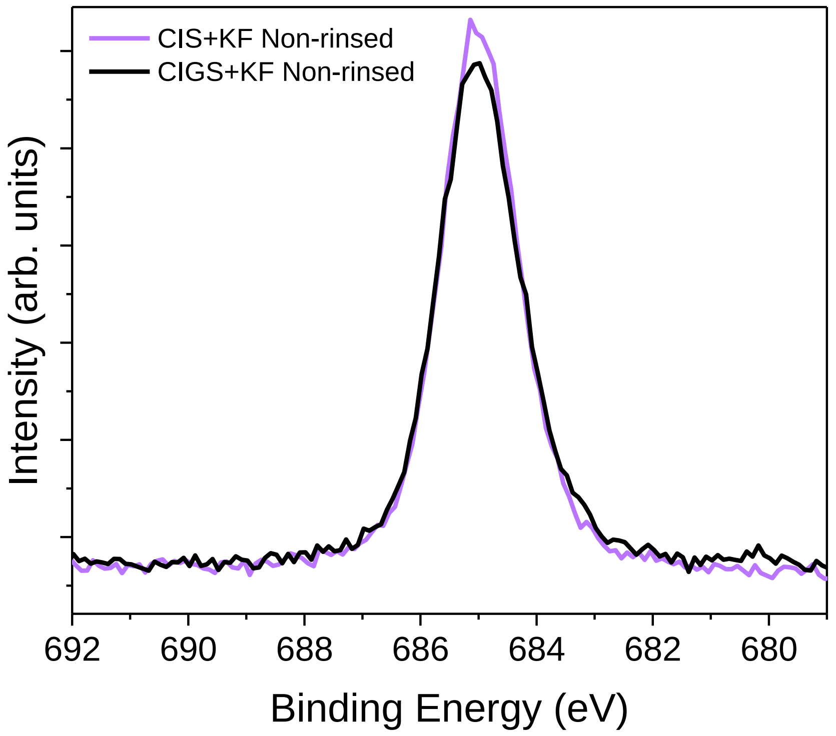
# *XPS F 1s of CIS+KF and CIGS+KF*




N. Valdes et al., *IEEE JPV*, p1846, 2019.

- Use XPS to understand differences in surface chemistry between CIGS+KF and CIS+KF
- F 1*s* spectra provides information on:
  - Intermediate chemistry after PDT and before CdS deposition
  - Proportional to K content without overlapping Auger lines

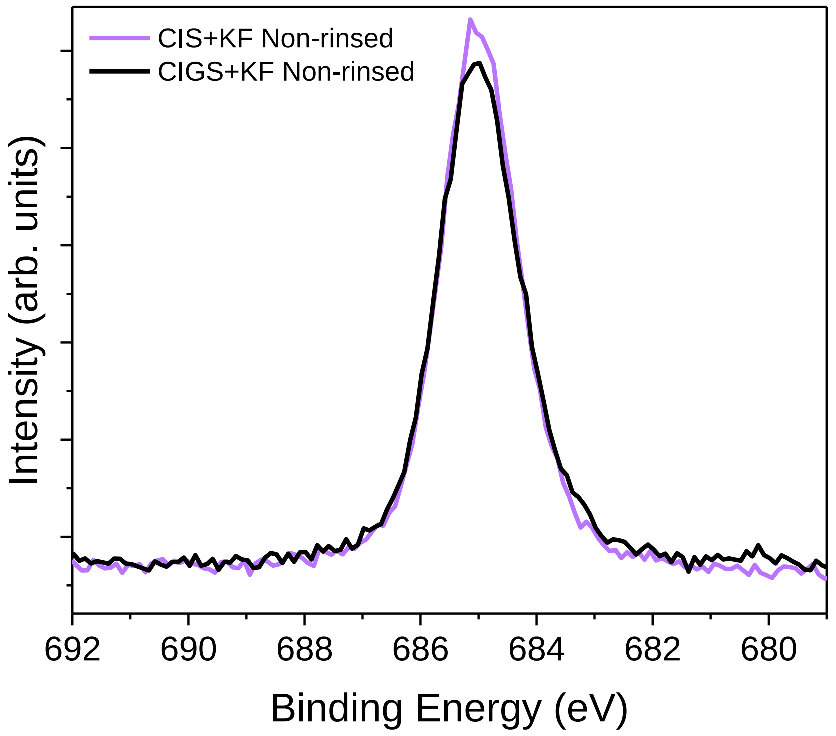
# XPS F 1*s* of CIS+KF and CIGS+KF




N. Valdes et al., *IEEE JPV*, p1846, 2019.

- Nearly identical F 1*s* peaks in non-rinsed CIS+KF and CIGS+KF
  - Ga does not affect KF content
  - Also see a similar intensity comparison in K 2*p*
- F 1*s* removed with water rinsing
  - F is on the surface as a water-soluble compound

# XPS F 1s of CIS+KF and CIGS+KF




N. Valdes et al., *IEEE JPV*, p1846, 2019.

| Candidate | Binding Energy (eV) |
|---|---|
| Measured F 1s | 685.0 |
| $GaF_3$ | 685.7 |
| $InF_3$ | 685.0 |
| KF | 684.0 |
| $CuF_2$ | 684.3 |


- M. Tabbal et al., *Mat. Res. Soc. Symp. Proc.*, 1992.
- Y. Kawamoto et al., *J. Fluorine Chem.*, 1999.
- W. Morgan et al., *J. Am. Chem. Soc.*, 1973.
- S. Gaarenstroom and N. Winograd, *J. Chem. Phys.*, 1977.

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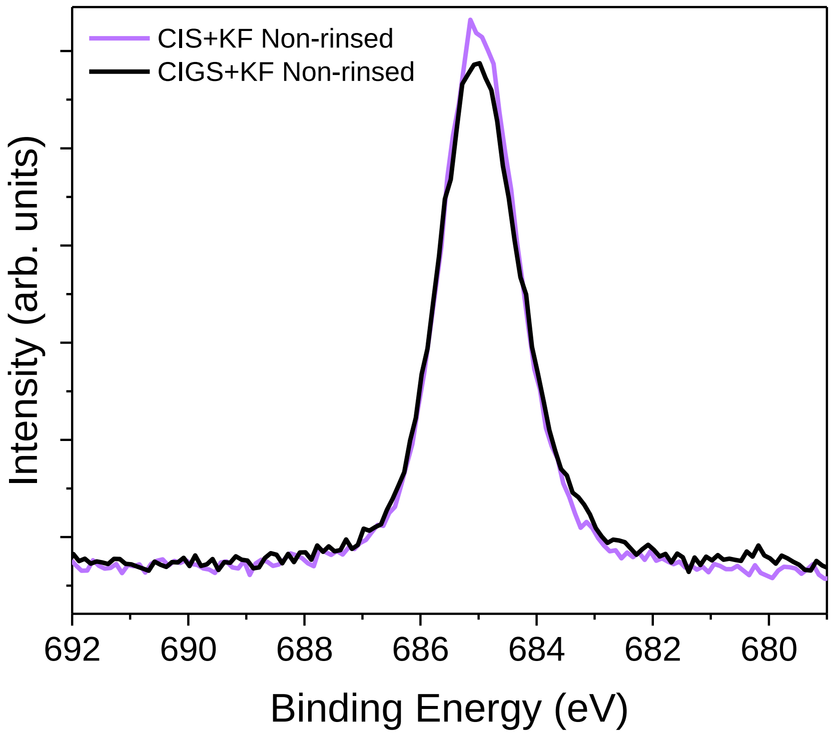


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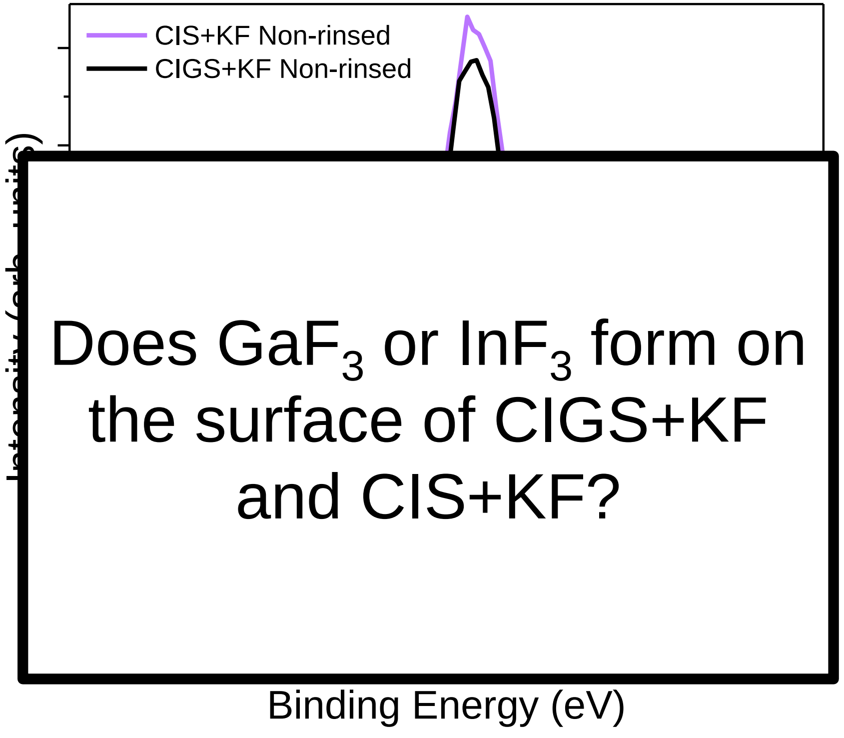


Does $GaF_3$ or $InF_3$ form on the surface of CIGS+KF and CIS+KF?

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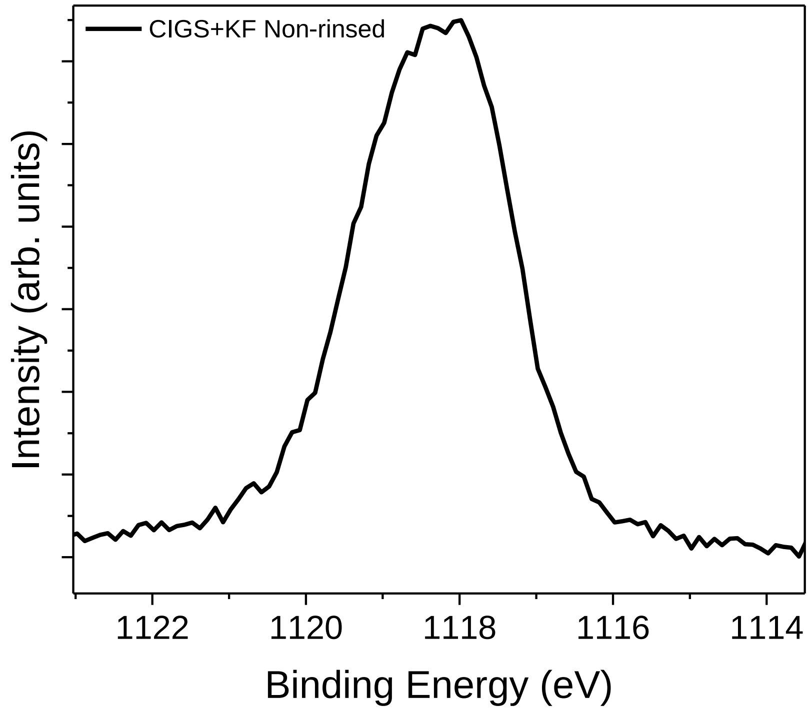


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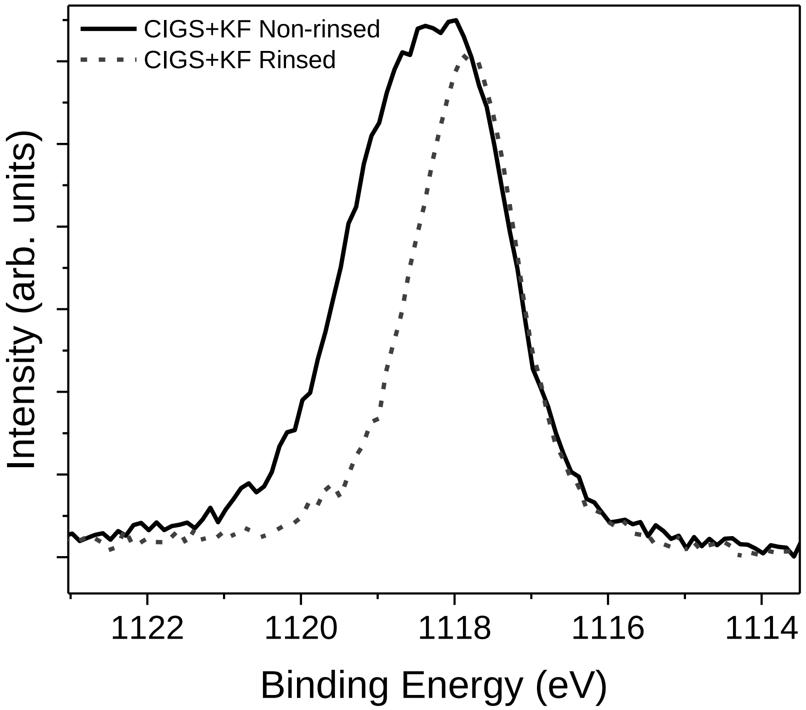


N. Valdes et al., *IEEE JPV*, p1846, 2019.

- Ga $2p_{3/2}$ narrows after rinsing
  - High GGI before rinsing
    - Baseline value afterwards
  - Removal of Ga with water rinsing

| Type | GGI |
|---|---|
| Non-rinsed | 0.47 |
| Rinsed | 0.28 |

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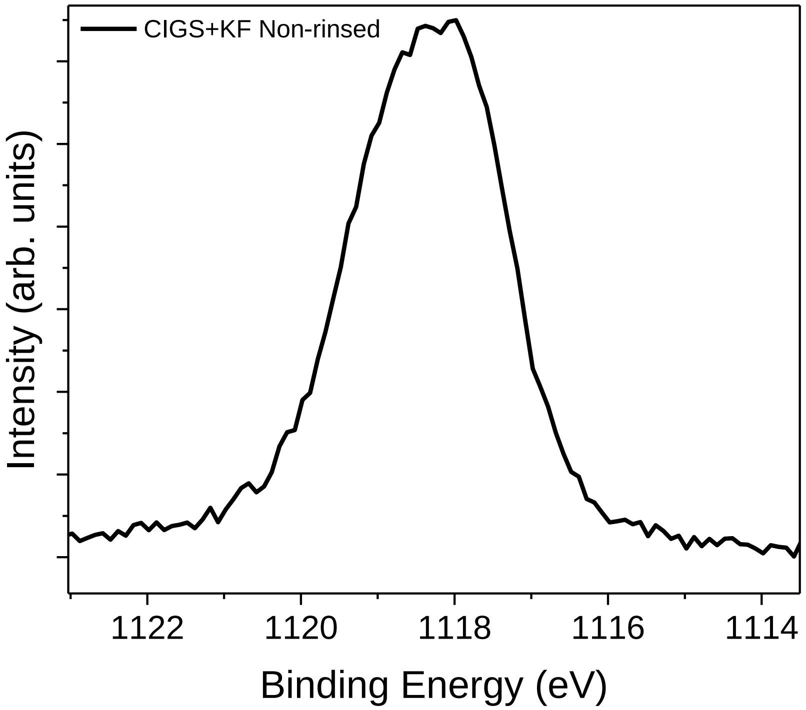


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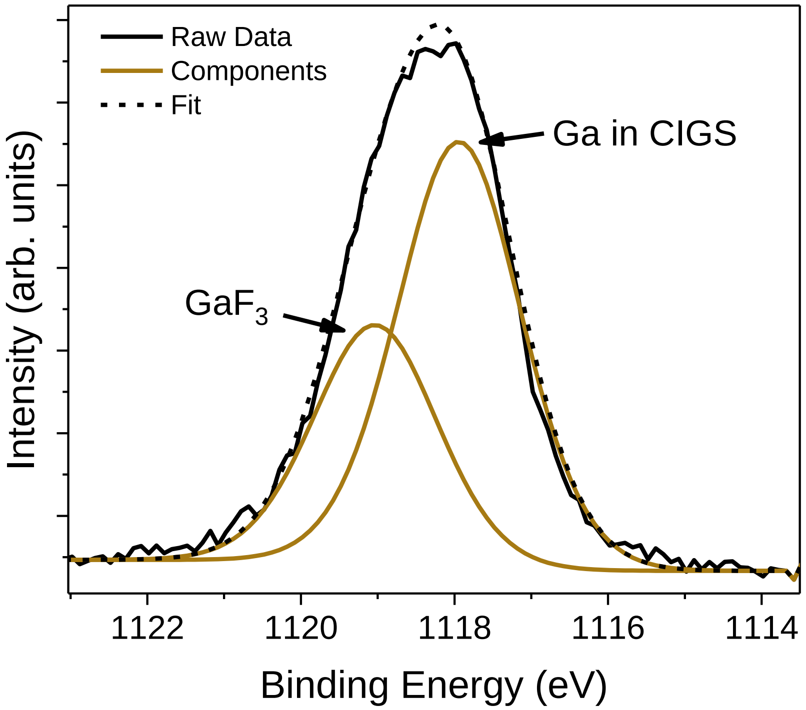


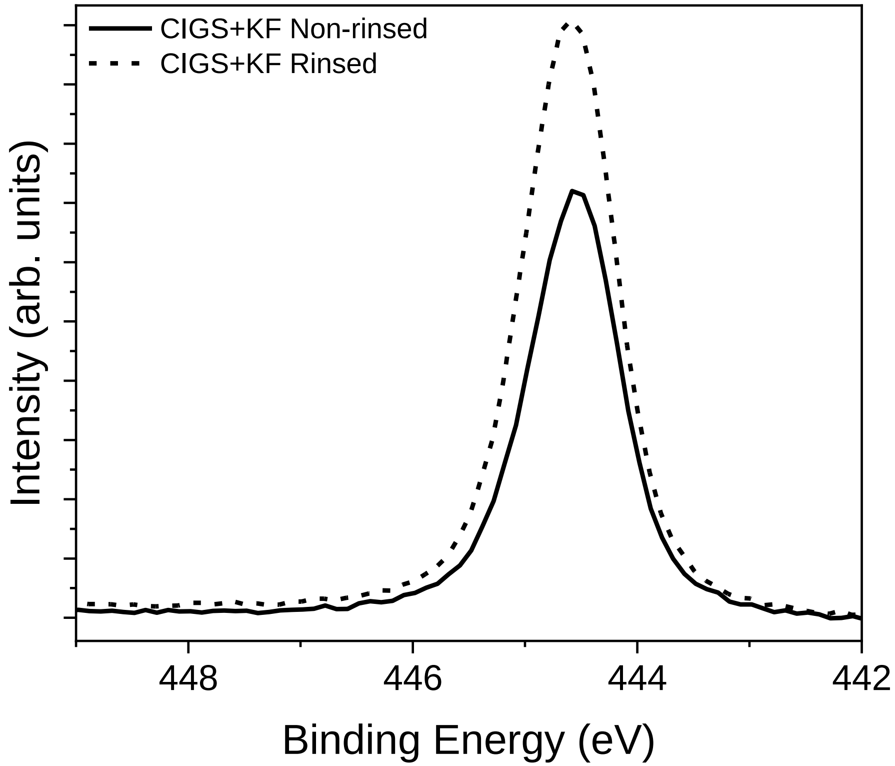

N. Valdes et al., *IEEE JPV*, p1846, 2019.

- Low binding energy peak: Ga in CIGS
  - Matches CIGS+KF rinsed and CIGS
- High binding energy peak: $GaF_3$
  - Also seen by Lepetit et al. in 2017

| Type | Binding Energy (eV) |
|---|---|
| Measured $GaF_3$ | 1119.0 |
| Literature $GaF_3$ | 1119.4 |

M. Tabbal et al., *Mat. Res. Soc. Symp. Proc.*, 1992.

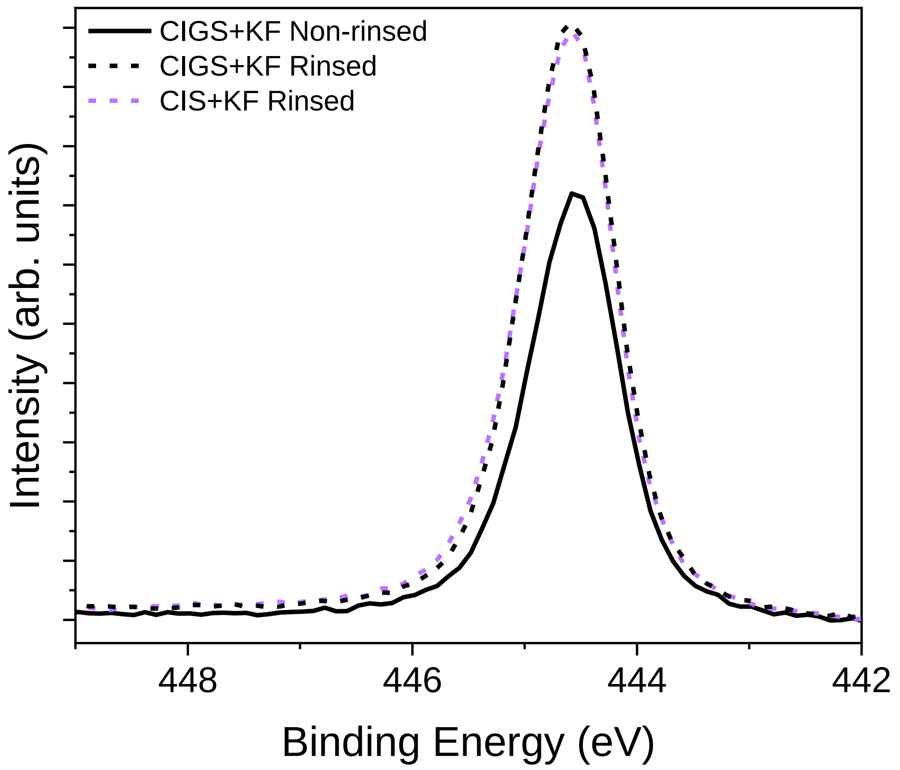
# *In 3$d_{5/2}$ CIGS+KF*




N. Valdes et al., *IEEE JPV*, p1846, 2019.

- Rinsed samples have higher intensity In 3*d* peaks
  - Surface layer that reduced XPS signal removed by water rinsing
    - Other elements' spectra also show this
- CIGS+KF does not show $InF_3$ peak

# *In 3d$_{5/2}$ of CIS+KF and CIGS+KF*

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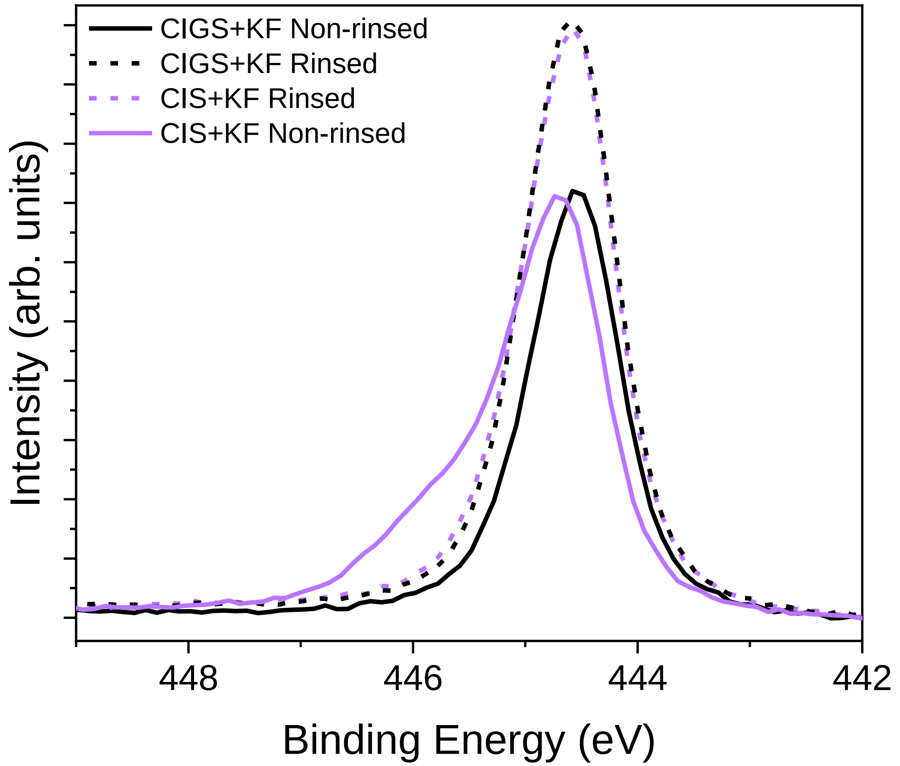


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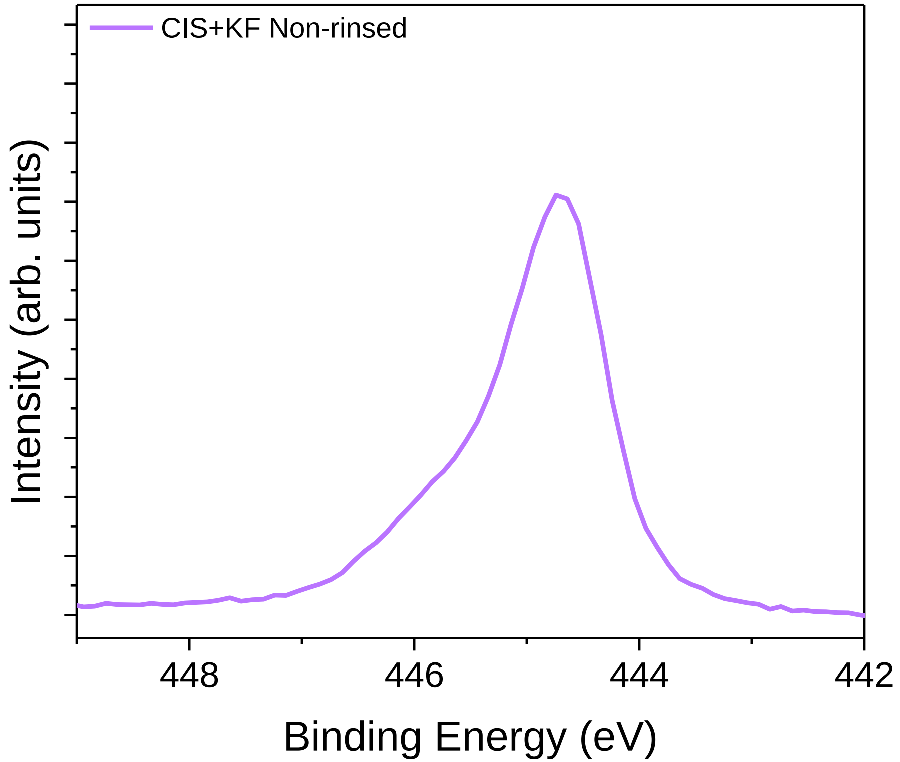
- CIGS+KF does not show $InF_3$ peak
- CIS+KF rinsed similar to CIGS+KF rinsed
- CIS+KF non-rinsed shows peak at higher binding energy

# *In 3d$_{5/2}$ of CIS+KF*




N. Valdes et al., *IEEE JPV*, p1846, 2019.

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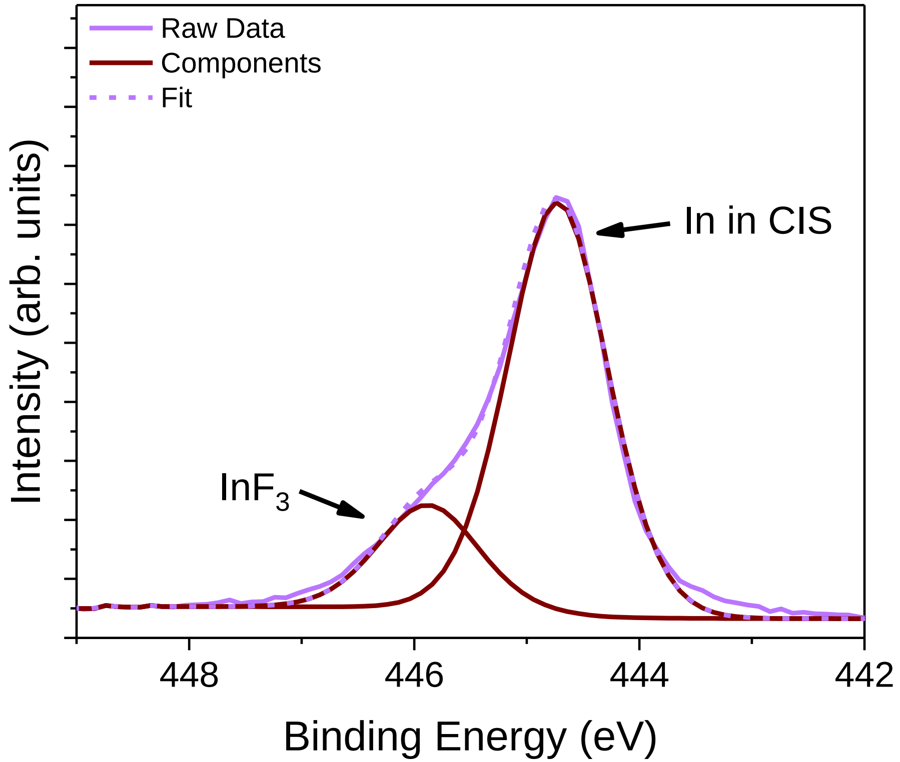


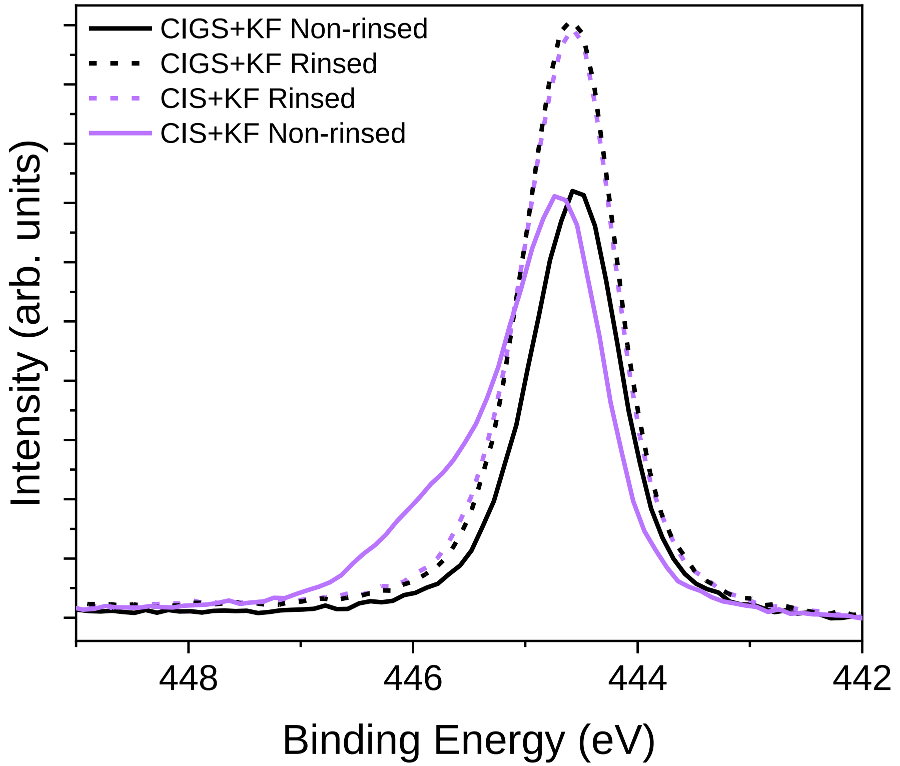

N. Valdes et al., *IEEE JPV*, p1846, 2019.

- Low binding energy peak: In in CIS
  - Matches CIS+KF rinsed and CIS
- High binding energy peak: $InF_3$

| Type | Binding Energy (eV) |
|---|---|
| Measured $InF_3$ | 445.9 |
| Literature $InF_3$ | 446.0 |

- T. Paul and D. Bose, *J. Appl. Phys.*, 1991.

# In $3d_{5/2}$ of CIS+KF and CIGS+KF

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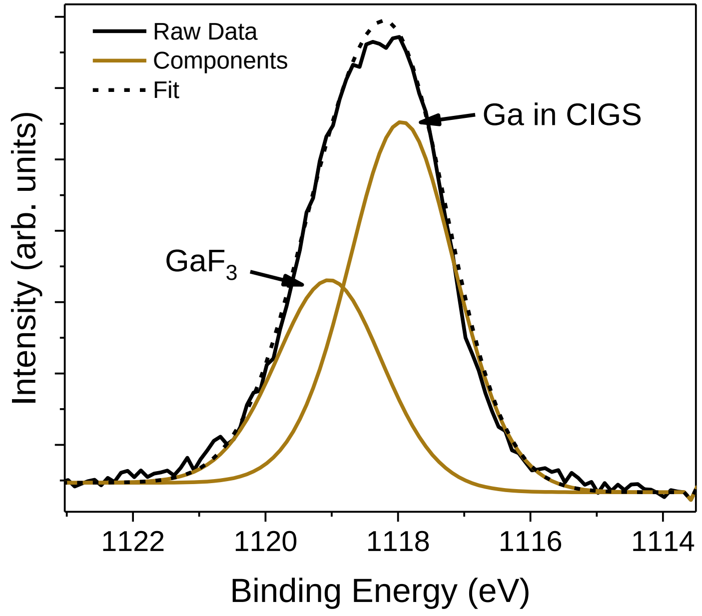
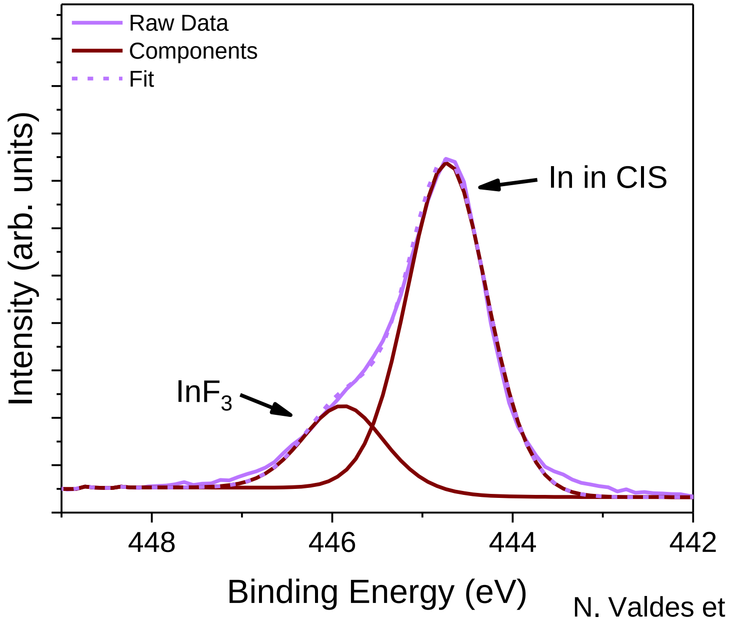
- $InF_3$ appears in CIS+KF non-rinsed
  - But not in CIGS+KF non-rinsed
- Preferential reaction:
  - F binds to In in CIS+KF
  - F binds to Ga in CIGS+KF

# Role of $GaF_3$ and $InF_3$ on Non-Rinsed Films




N. Valdes et al., *IEEE JPV*, p1846, 2019.

- $GaF_3$ or $InF_3$ are products of KF reaction with Cu-deficient CIGS
  - Could be $K(In,Ga)F_4$ and $K_3(In,Ga)F_6$ (exist, but no XPS information found)
- $GaF_3$ or $InF_3$ → no effect on performance as they are removed during CdS deposition
- Not clear if removal of surface Ga via $GaF_3$ alters surface electronic properties

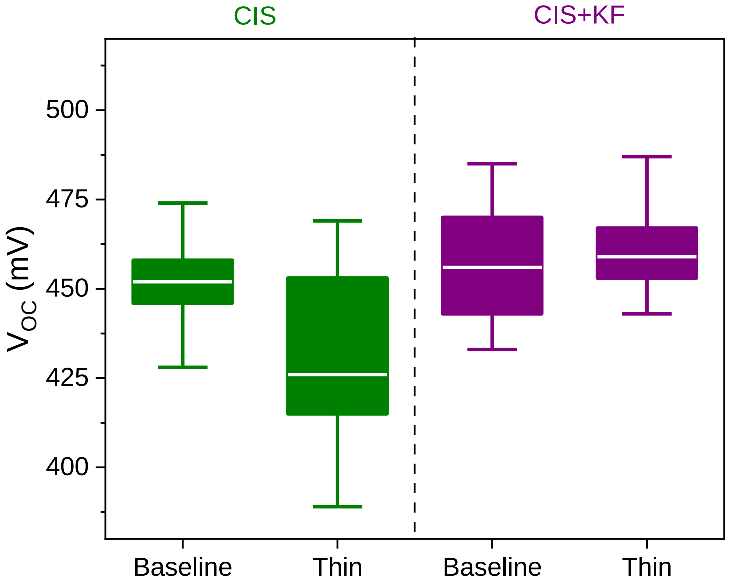
# *Cu Composition Reduction Due to KF-PDT*

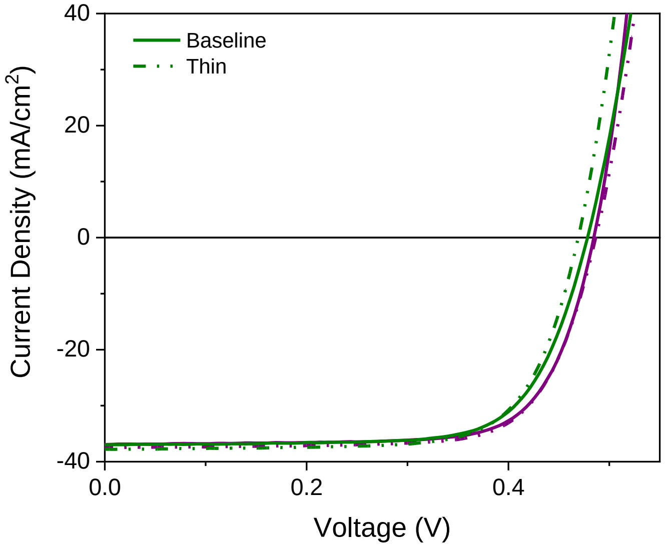
| Type | % Reduction Cu 2*p* XPS Peak Area |
|---|---|
| CIS → CIS+KF | 35 |
| CIGS → CIGS+KF | 51 |

Samples were water rinsed.
N. Valdes et al., *IEEE JPV*, p1846, 2019.

- Alkali-PDTs known to reduce Cu content on the surface
- Ga containing films have larger decrease in surface Cu concentration due to KF
  - Is it due to Ga chemistry, or a morphology effect?
  - Might explain “depletion” in surface Cu with KF

# KF Effect on CIS $V_{OC}$

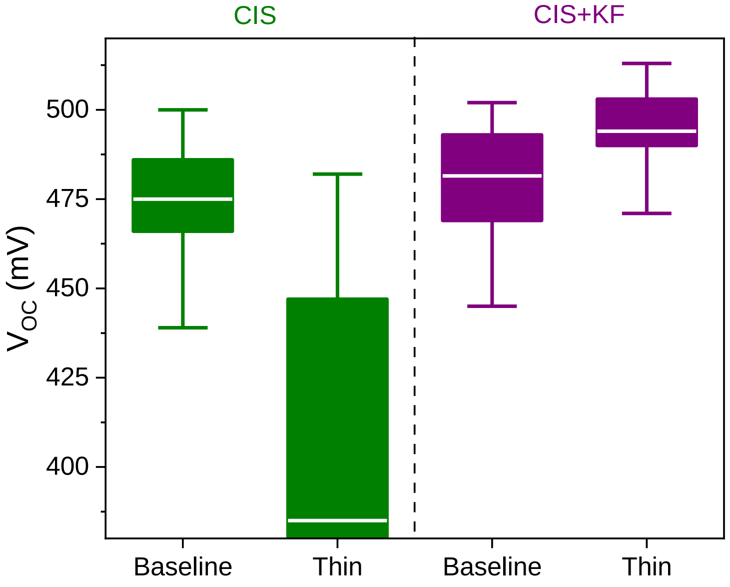


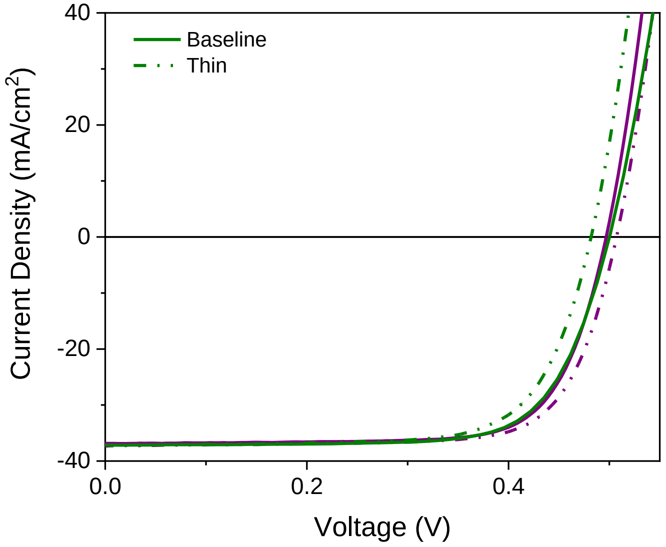




- KF shows similar $V_{OC}$ trends with or without Ga
  - Focus on low $E_g$ case, CIS
- Baseline CdS (50 nm):
  - CIS and CIS+KF → Similar $V_{OC}$
- Thin CdS (35 nm):
  - Reduced $V_{OC}$ in CIS
  - No $V_{OC}$ reduction in CIS+KF
    - Improved CdS growth

N. Valdes et al., *IEEE JPV*, p906, 2019.

# KF Effect on CIS $V_{OC}$ After Heat Treatment

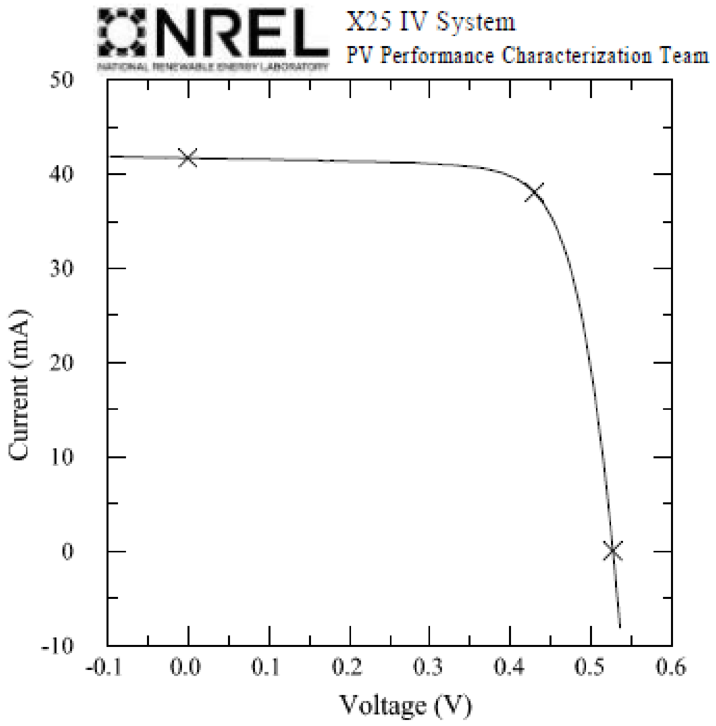



- Some devices received 2 min. 200°C heat treatment in air after initial test
- All types get $V_{OC}$ boost except CIS with thin CdS
- CIS+KF with thin CdS: $V_{OC}$ > 500 mV
- Heat treatment critical for high efficiency CIS+KF

N. Valdes et al., *IEEE JPV*, p906, 2019.

# *High Efficiency CIS+KF*




$V_{oc}$ = 0.52606 ± 0.00084 V
$I_{sc}$ = 41.70 ± 0.26 mA
$J_{sc}$ = 40.96 ± 0.27 mA/cm$^2$
Fill Factor = 74.43 ± 0.27 %

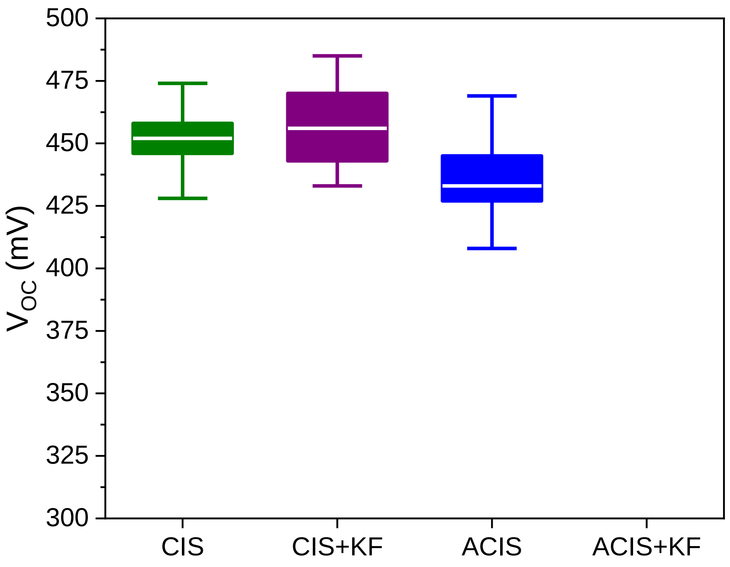
$I_{max}$ = 38.05 ± 0.23 mA
$V_{max}$ = 0.428995 ± 0.000060 V
$P_{max}$ = 16.33 ± 0.10 mW
Efficiency = 16.04 ± 0.11 %

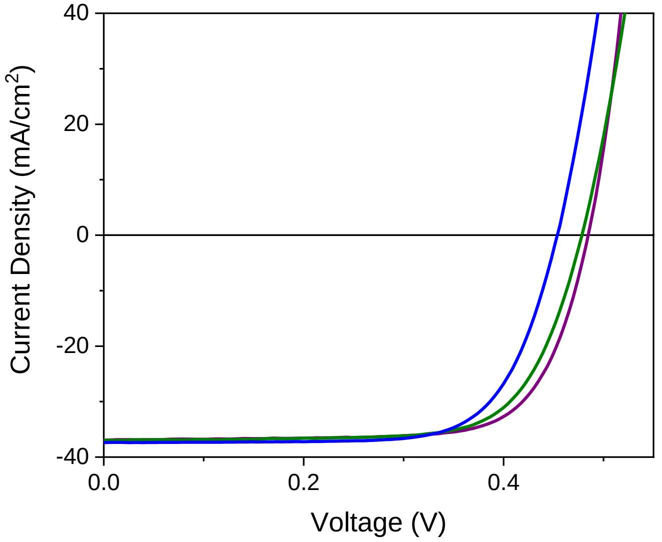
Storage State

N. Valdes et al., *IEEE JPV*, p906, 2019.

- Deposited $MgF_2$ anti-reflection coating on best cells
- Best cell η = 16.0%
  - Record $CuInSe_2$ solar cell
- KF → higher efficiency CIGS for range of Ga content
- Are high efficiencies also possible in ACIS+KF?

# $V_{OC}$ Comparison



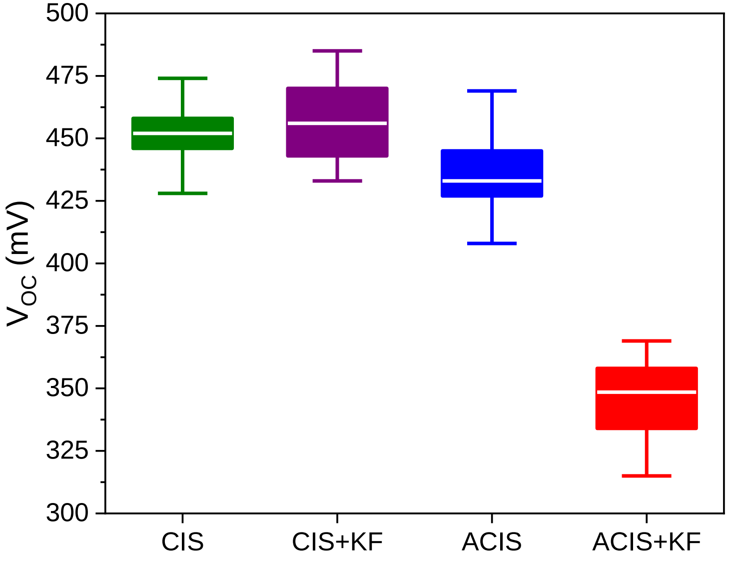



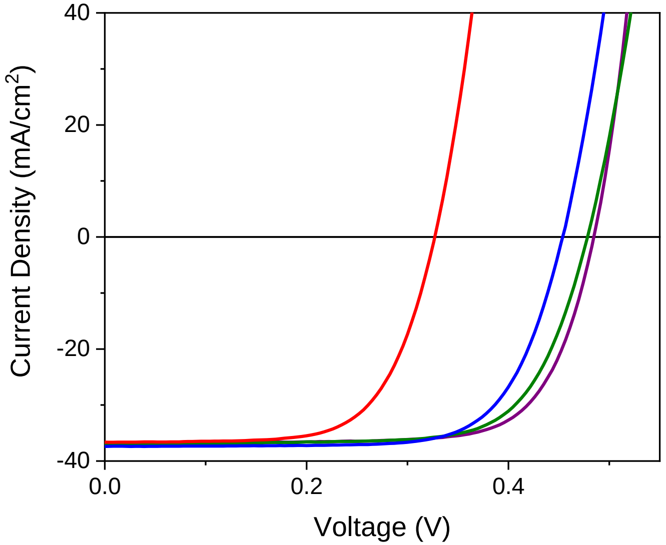

- ACIS has lower $V_{OC}$ than CIS
  - Low carrier concentration in best devices
  - But makes up for $V_{OC}$ reduction by improved current collection (Valdes et al. 2019)

Baseline CdS.
Devices were not heat treated.

N. Valdes et al., *IEEE JPV*, p906, 2019.

# $V_{OC}$ Comparison




- ACIS+KF has very low $V_{OC}$
- $V_{OC}$ reduction independent of KF thickness from 0.5 nm to 15 nm
- Uppsala U. → reduced KF amounts required in ACIGS (Edoff et al. 2017, Donzel-Gargand et al. 2018)

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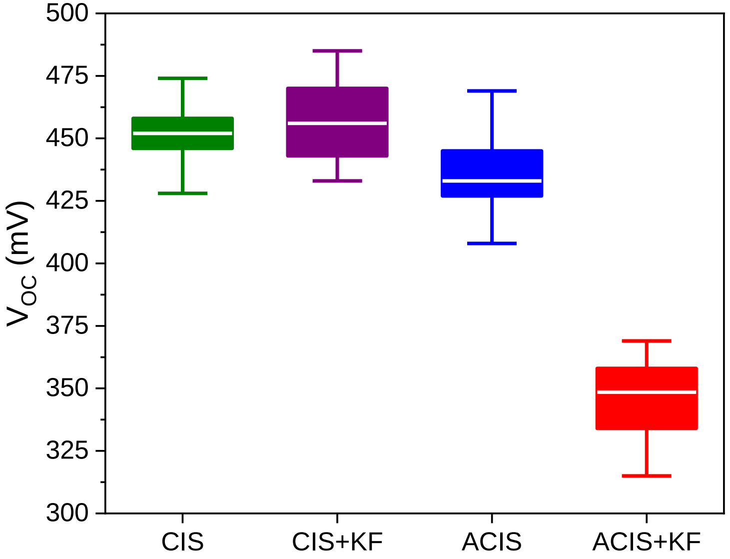


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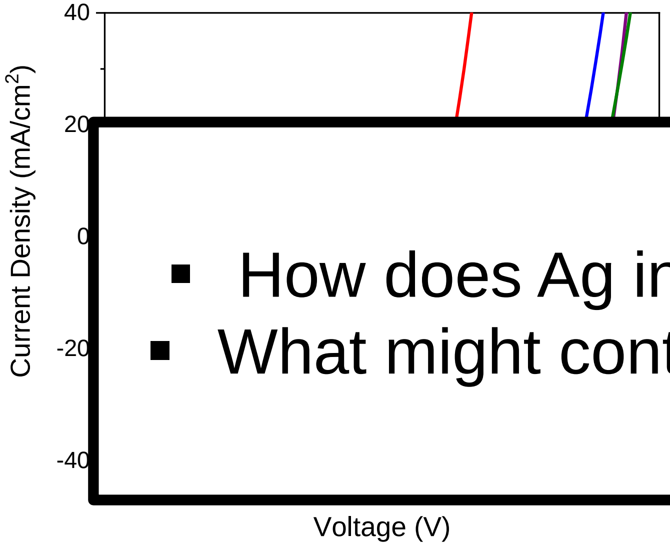



- How does Ag influence the KF-PDT on ACIS?
- What might contribute to $V_{OC}$ loss in ACIS+KF?

N. Valdes et al., *IEEE JPV*, p906, 2019.

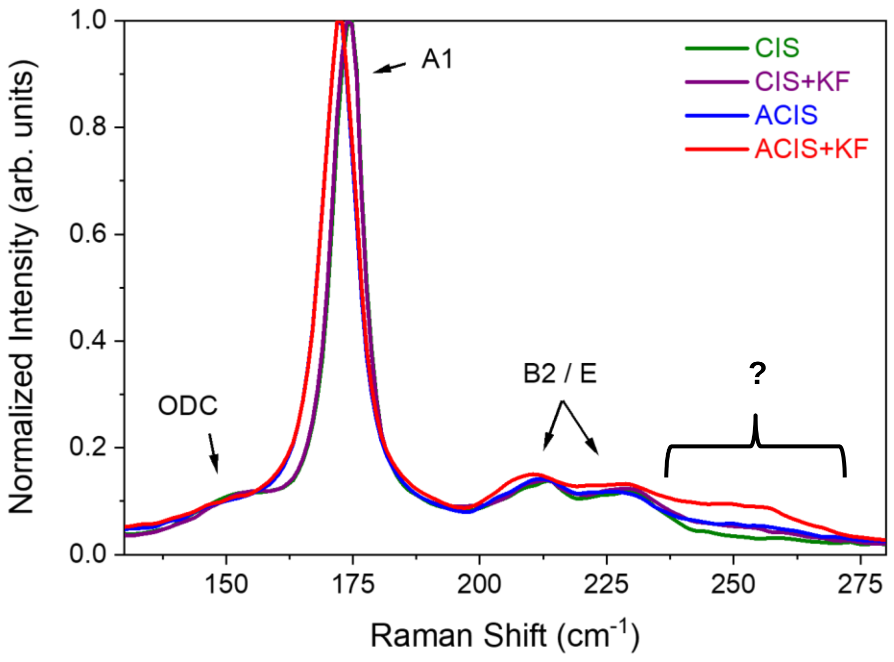
# Group 1 Composition Reduction Due to KF by XPS

| Type | Element | % Reduction XPS Peak Area |
|---|---|---|
| CIS → CIS+KF | Cu | 35 |
| ACIS → ACIS+KF | Cu | 42 |
| ACIS → ACIS+KF | Ag | 25 |

Samples were water rinsed.
N. Valdes et al., *IEEE JPV*, p1846, 2019.

- Ag decreases less than Cu with KF-PDT
  - Also seen by Donzel-Gargand et al. 2018 in ACIGS
- Additional observations by XPS for ACIS and ACIGS:
  - No change in surface K or F content or binding energy
  - $InF_3$ in ACIS+KF and $GaF_3$ in ACIGS+KF still present in non-rinsed samples

# Raman Spectroscopy of Bare Absorber Layers

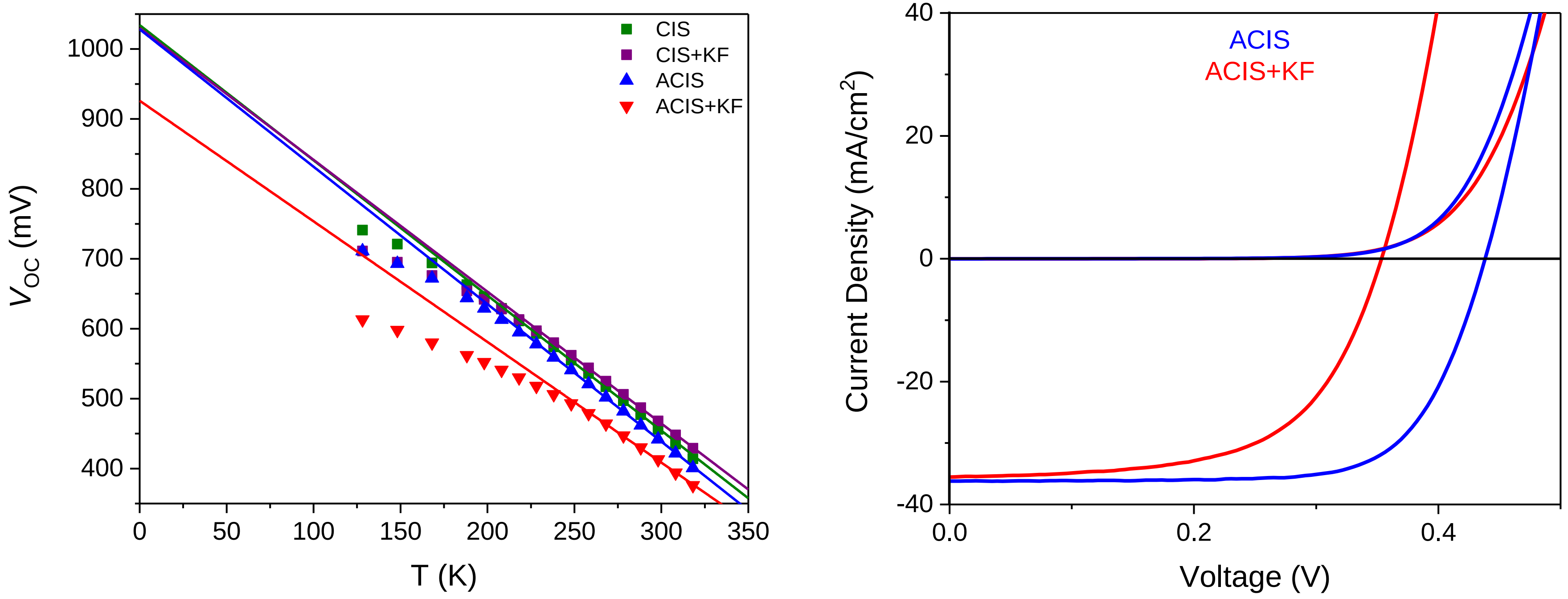



N. Valdes et al., *IEEE JPV*, p906, 2019.

- Broad peak ~255 $cm^{-1}$ for ACIS+KF
- Not identified by Raman or GIXRD
- Possible candidates:
  - α-$In_2Se_3$ = 255 $cm^{-1}$
  - $Cu_2Se$ = 260 $cm^{-1}$
- Regardless, different surface exists for ACIS+KF
- Still present after water rinse or chemical etch
  - e.g. HCl, KCN, $NH_4OH$

# *Features of ACIS+KF Devices*

- ACIS+KF demonstrates lower $E_a$ compared to other devices
  - Interface recombination dominates in these devices
- Light to dark crossover observed in *J-V* of ACIS+KF
  - Maybe related to photoconductivity in the CdS layer




N. Valdes et al., *IEEE JPV*, p906, 2019.

# Comparison of Best Cell Baseline vs. Thin Buffers

| Type | Baseline CdS $V_{OC}$ (mV) | Thin CdS $V_{OC}$ (mV) | Thin - Baseline $V_{OC}$ (mV) |
|---|---|---|---|
| CIS | 482 | 469 | - 13 |
| CIS+KF | 485 | 487 | + 2 |
| ACIS | 455 | 458 | + 3 |
| ACIS+KF | 411 | 436 | + 25 |

Devices were not heat treated
N. Valdes et al., *IEEE JPV*, p906, 2019.

- Reduced CdS thickness:
  - CIS has decreased $V_{OC}$ likely due to incomplete CdS coverage
  - No change in $V_{OC}$ for CIS+KF or ACIS
  - Large improvement in $V_{OC}$ in ACIS+KF

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N. Valdes et al., *IEEE JPV*, p906, 2019.

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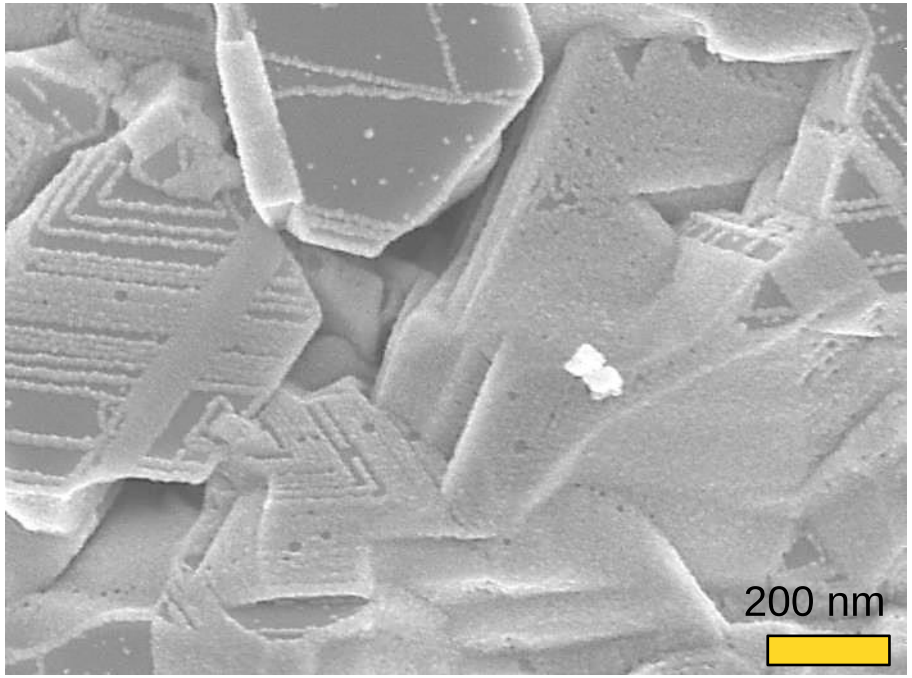
Does CdS grow differently due to KF and/or Ag alloying?

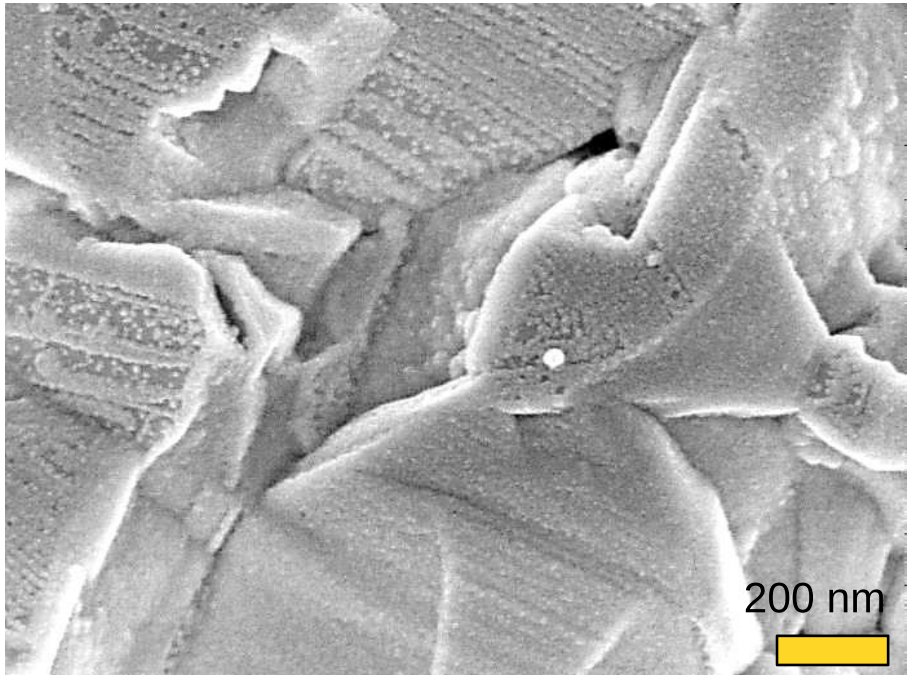
# SEM with 10 nm CdS Overlayer

CIS




- Incomplete coverage on some grains
  - Related to {112} oriented grains (Witte et al. 2013)
  - Metal or anion terminated

CIS+KF

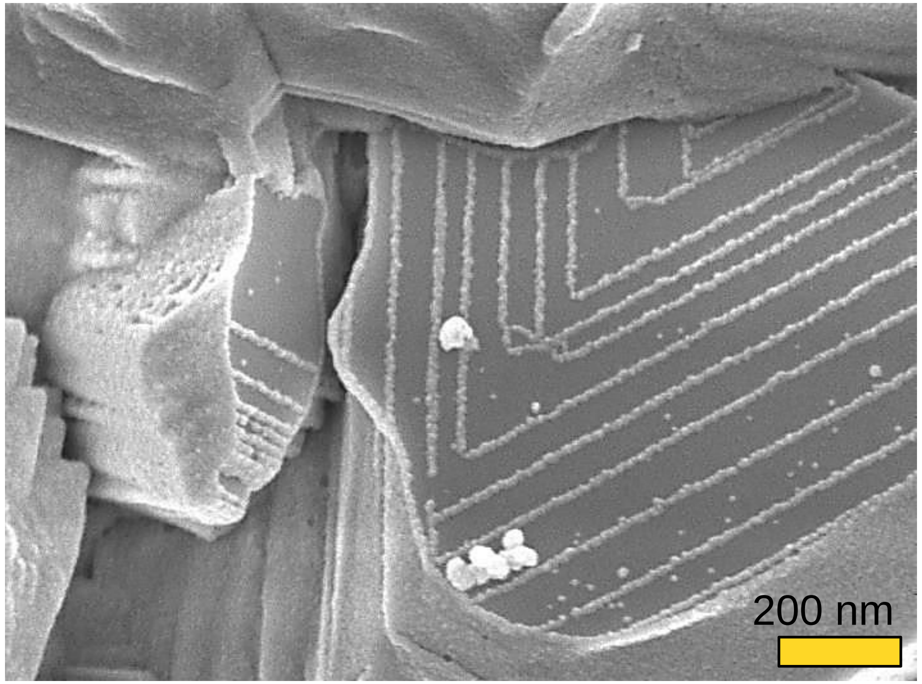



- Improved coverage due to KF

N. Valdes et al., *IEEE JPV*, p906, 2019.

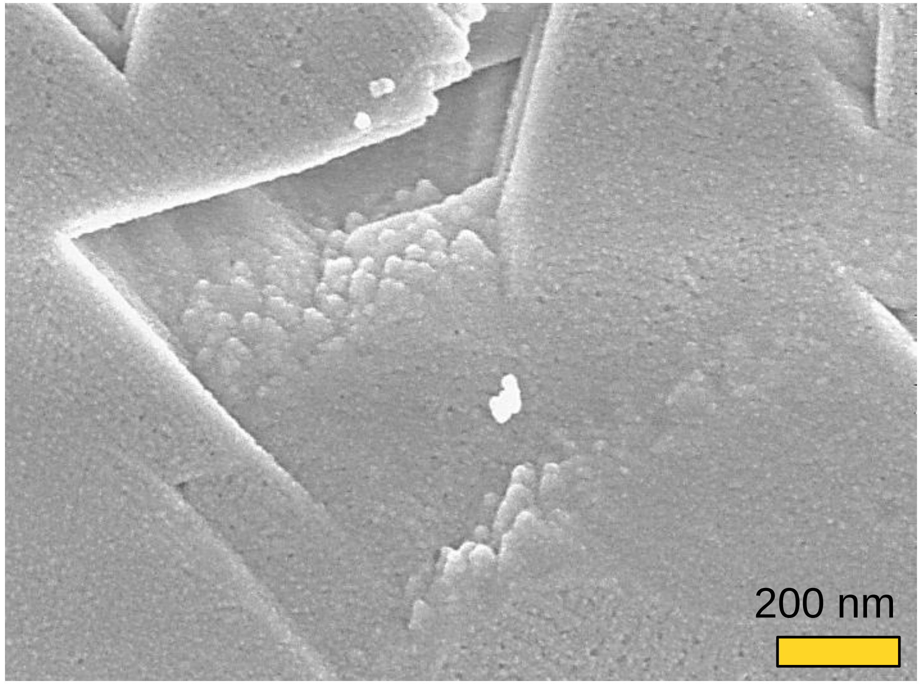
# SEM with 10 nm CdS Overlayer

ACIS




- Large grains with incomplete coverage
  - Perhaps same as CIS but on a larger scale

ACIS+KF




- Complete coverage even with 10 nm CdS
  - Increased Cd and S seen by XPS (Valdes et al. 2019)
- KF causes different nucleation

N. Valdes et al., *IEEE JPV*, p906, 2019.

Do we see similar trends with RbF-PDT?

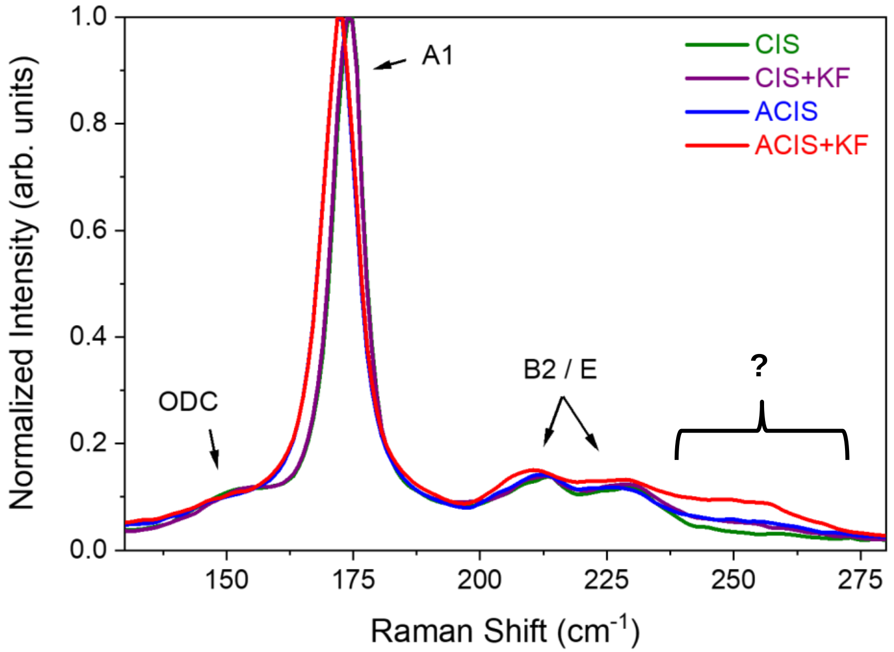
# How Do Best Cell Results Compare with RbF?

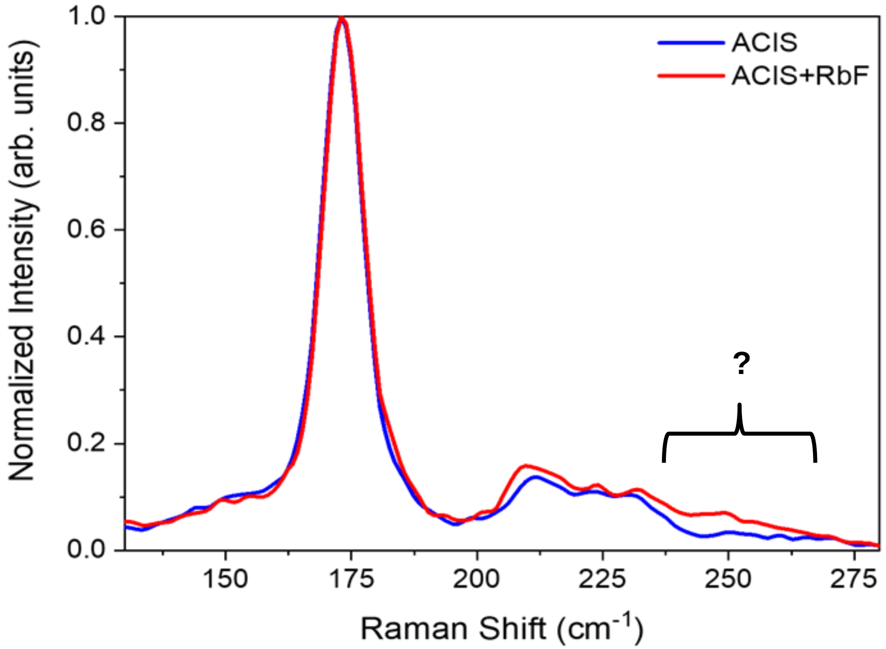
| Type | Baseline CdS $V_{OC}$ (mV) | Thin CdS $V_{OC}$ (mV) | Thin - Baseline $V_{OC}$ (mV) |
|---|---|---|---|
| CIS | 482 | 469 | - 13 |
| CIS+RbF | 482 | 477 | - 5 |
| ACIS | 455 | 458 | + 3 |
| ACIS+RbF | 362 | 386 | + 24 |

Devices were not heat treated

- RbF *J*-*V* results → similar trends to KF:
  - CIS+RbF:
    - Comparable $V_{OC}$ to CIS (with no heat treatment)
    - Reduced $V_{OC}$ loss with thin CdS
  - ACIS+RbF:
    - Decreased $V_{OC}$ vs. ACIS
    - Large increase in $V_{OC}$ with thinner CdS

# Raman Spectra of Bare Absorber Layers




N. Valdes et al., *IEEE JPV*, p906, 2019.

- Unidentified peak also exists in ACIS+RbF
  - Both KF and RbF lead to a modified surface in ACIS+alkali-PDT

# Summary (1/2)

- Investigated alkali-PDTs on CIS and the influence of Ga and Ag
- Studied the XPS properties of CIS vs. CIGS
  - Ga does not change the amount of K or F on surface
  - Group III fluorides are products of KF reaction
  - Preferential reaction occurs in which
    - CIGS+KF → $GaF_3$
    - CIS+KF → $InF_3$
  - CIGS has larger decrease in Cu on surface after KF
- CIS+KF devices:
  - Tolerate reduced CdS thickness
  - Have high efficiencies after heat treatment
    - $\eta$ = 16.0% for CIS without Ga

# Summary (2/2)

- ACIS+KF leads to devices with low $V_{OC}$
- ACIS+KF has properties unique from other absorbers in this work:
  - Less Ag reduction at surface compared with Cu
  - Unidentified peak at 255 $cm^{-1}$ in Raman spectra
  - Dominant interface recombination
  - Light to dark crossover
  - Different CdS growth
- RbF-PDT gives similar *J*-*V* and Raman results for both CIS and ACIS

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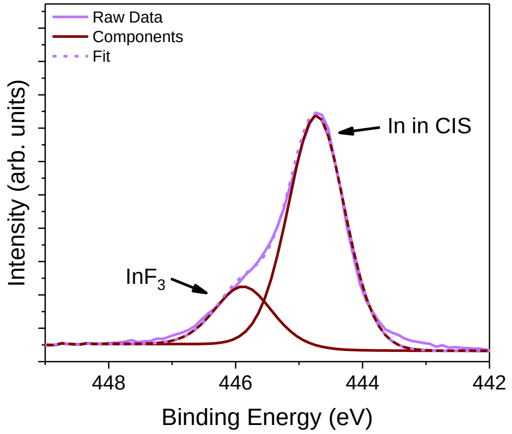
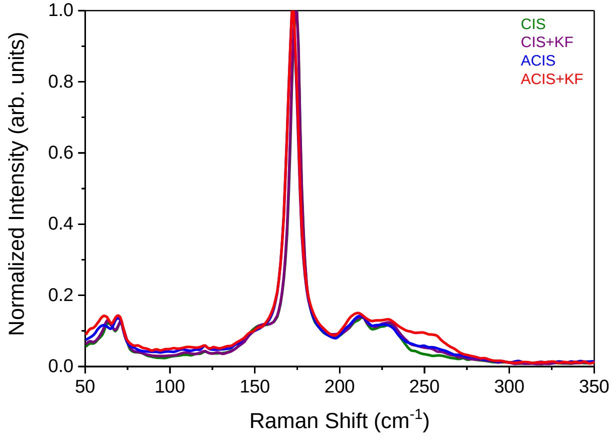
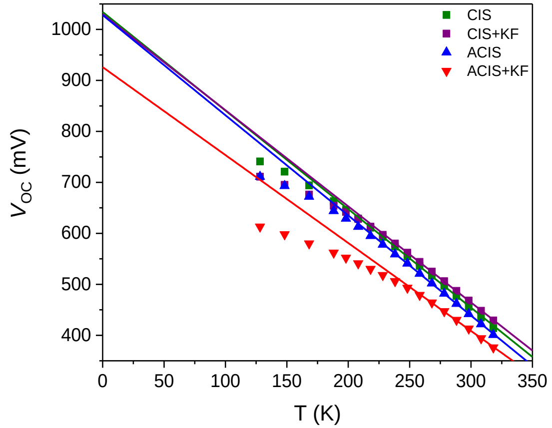
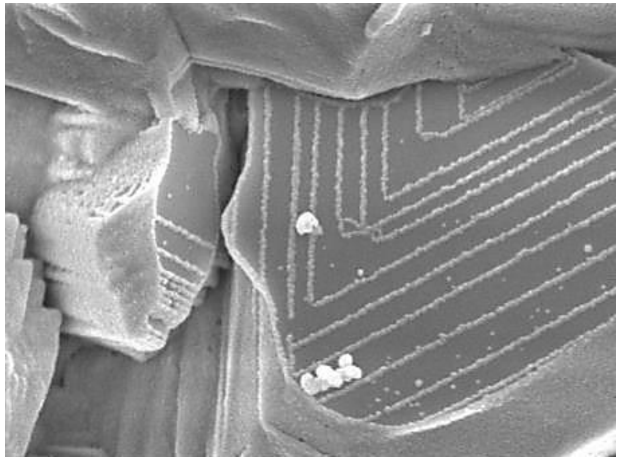
- Discussion and technical support of IEC and UD colleagues, past and present:
  - Wayne Buchanan
  - Shannon Fields
  - Jason Anderson
  - Kevin Dobson
  - Christopher Thompson
  - Kevin Jones
  - Robert Opila
  - Yong Zhao



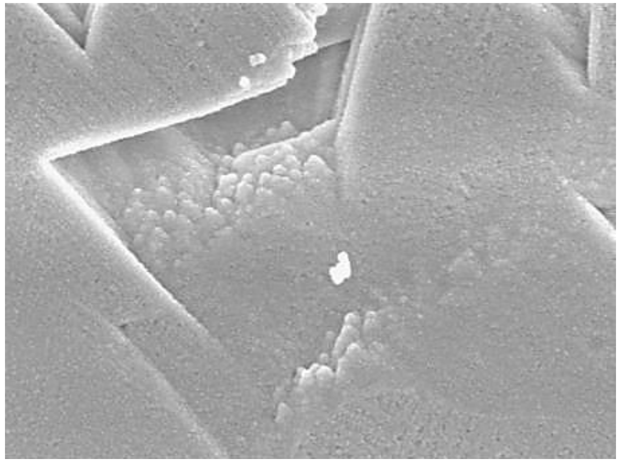




# Thank you!



Questions?



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